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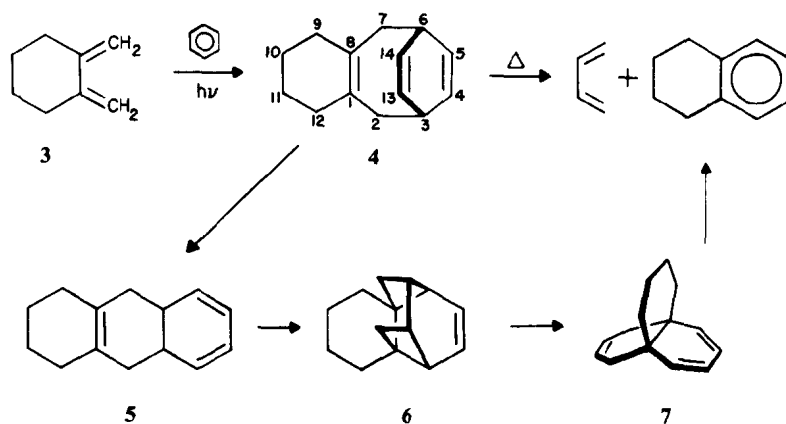
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Chapter 1

AN ANIMAL IS A CHEMIST'S BEST FRIEND

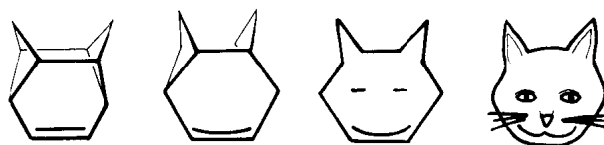
Andrew Gilbert and co-workers at England's University of Reading irradiated a mixture of 1,2-dimethylenecyclohexane (**3**) and benzene, and they obtained the tricyclic triene **4**.¹ We understand this [4 + 4] cycloaddition, induced by light, in terms of the famous Woodward–Hoffmann rules of orbital symmetry.² When Dr. Gilbert and research colleague Robin Walsh³ subsequently heated **4**, some of it simply reverted to **3** and benzene. (This reversal, if concerted, was “symmetry-forbidden”; orbital symmetry demands that a photochemical process should go into reverse photically but not thermally. Forbidden reactions do occur but with low probability.) The rest of the [4 + 4] adduct produced 1,2,3,4-tetrahydronaphthalene (tetralin) and 1,3-butadiene. To



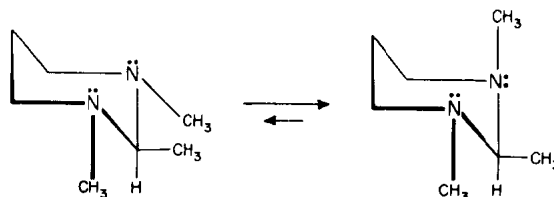
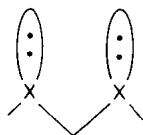
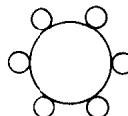
account for these last two products, the Reading researchers proposed a mechanism in step with the Woodward–Hoffmann canons. Thus, triene **4** gets to **5** by a 1,3-sigmatropic shift of C7 (from C6 to C13); the statutes would require inversion at C7. The convolution of **5** \rightarrow **6** proceeds via intramolecular [4 + 2] (Diels–Alder) cycloaddition. The remaining two steps (**6** \rightarrow **7** \rightarrow products) are retro Diels–Alder reactions.

Seeking a name for the unusual polycycle **6**, Gilbert and Walsh held a friendly competition in their research group.⁴ A student, David A. Smith, mentally discarded the ring at the left, rotated the rest by 90°, and visualized the parent olefin **8**. A few more

imaginative jumps transformed **8** into the face of a smiling cat, and so “felicene” for **8** was born. (*Felis* is Latin for “cat.”) David Smith won the competition paws down!

**8**

Felicene’s ears evolved from carbon bridges. But in Notre Dame, Indiana, they grew ears from lonesome electron pairs. In 1968, a team led by Ernest Eliel, then at the University of Notre Dame, discovered that the conformational equilibrium **9** \rightleftharpoons **10** preferred a chair with one axial N-methyl and one equatorial N-methyl, rather than with two equatorial N-methyls. They thought that repulsion between lone pairs on the two nitrogens might be a factor that disfavors **9**. When Professor Eliel discussed this “effect” at Dundee, Scotland, he drew the orbitals on a blackboard for a colleague. The next day the drawing (which resembled **11**) was still there, but some wag had written “brer rabbit” alongside it.⁵ Our earnest chemist was amused by the notion of a “brer rabbit effect” and finally chose the modified expression “rabbit-ear” effect to describe destability brought on by parallel (i.e., *syn*-axial) orientation of unshared pairs on nonadjacent atoms.⁶ However, Dr. Eliel’s researchers later presented evidence that,

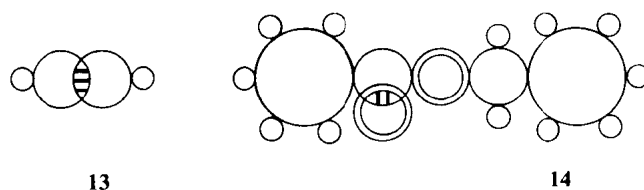
**9****10****11****12**

in fact, rabbit-ears contribute only in a minor way to the free-energy difference between **9** and **10**.⁷ Some theoreticians think it’s because the ears are clipped, i.e., a lone pair orbital on nitrogen is actually quasi-spherical and, therefore, nondirectional. In a theoretical study of the “anomeric effect,”* Saul Wolfe (Queen’s University, Canada), Arvi Rauk (also then at Queen’s), Luis Tel (Universidad de Valladolid, Spain), and Imre Csizmadia (University of Toronto) concluded that “the ‘rabbit-ear’ effect is actually an example of the well known Harvey phenomenon.”¹² “Harvey” is the fictitious invisible rabbit in a stage play by Mary Chase.¹³ And Dr. Wolfe learned about the play from a

*Raymond Lemieux adopted the phrase “anomeric effect” in 1959 when he was at the University of Ottawa.^{8,9} Professor Lemieux, co-workers Paul Chü and Rudy Kullnig, and collaborating spectroscopists Harold Bernstein and William Schneider (National Research Council Laboratory at Ottawa) pioneered the use of ¹H NMR to study sugars and sugar derivatives. Among other things, they observed that axial anomers possess unexpected stability and attributed this “anomeric effect” at C1 to a stereoelectronic property of the acetal linkage.^{10,11}

Queen's chemistry graduate student who was at that time moonlighting in a local summer production of *Harvey*.¹⁴ The theorists pointed out that a spherical lone pair is likewise "invisible" from a stereochemical standpoint. (Trust theoreticians to help us view things more accurately but see them less clearly!)

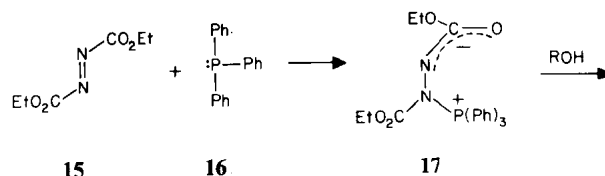
Incidentally, chemical lobes did not begin at the University of Reading or at Notre Dame. In fact, symbol **12** drawn by Austrian physicist Joseph Loschmidt in 1861 to represent benzene unmistakably augured an "eary" future for chemistry.¹⁵ According to science historians, Loschmidt used small circles for hydrogen, larger ones for carbon, two concentric circles for oxygen, and three concentric ones for nitrogen. In a booklet published in Vienna in 1861, and titled *Konstitutions Formeln der organischen Chemie in graphischer Darstellung*, *Chemische Studien, I*, Loschmidt, with keen insight, wrote out over 360 structures for organic compounds; these included **12** for benzene, **13** for acetylene, and **14** for benzyl benzoate. His cyclic formula for benzene resembles, at least superficially, the ring structure proposed by Friedrich August Kekulé four years (!)

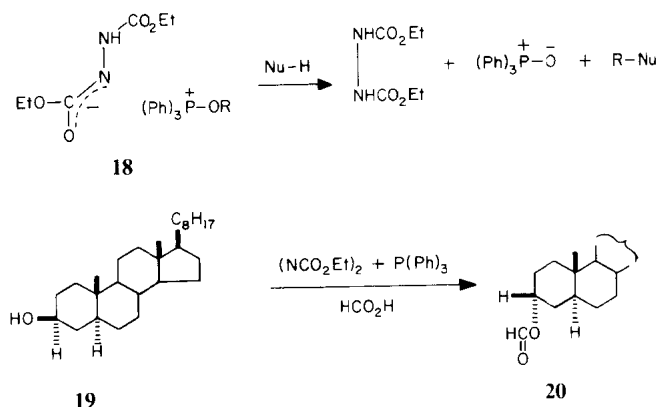


later. Because of its small circulation, Loschmidt's brochure went virtually unnoticed; and August Kekulé (he used only his second given name) emerged as champion of the benzene ring.¹⁶ By the way, even though the Kekulé name has an acute accent on the final e, the family was of Czech and not French origin. It seems that August Kekulé's father, Ludwig, was employed in Hesse, a grand duchy in southwest Germany at that time under the patronage of France. Ludwig added the accent, probably to keep the French from mispronouncing his name "Kekyl."¹⁷

Oyo Mitsunobu's research with diethyl azodicarboxylate (**15**) and triphenylphosphine (**16**), conducted initially at Tokyo Institute of Technology and then at Tokyo's Aoyama Gakuin University, has spawned some very useful chemistry.¹⁸ These two reagents combine to form a salt (**17**) that effectively activates alcohols toward S_N2 -type displacement by external or internal nucleophiles. The reaction, which may proceed via an alcohol-salt complex (**18**) or via pentavalent phosphorus species,^{18c} has broad scope.¹⁹ For example, the conversion, in 97% yield, of the steroidal 3β -ol **19** to the 3α -ol formate **20**,²⁰ developed in Ajay Bose's laboratory at Stevens Institute of Technology, is but one of its many applications.

Mitsunobu and his colleagues could hardly have guessed that their versatile reaction would acquire different nicknames. Chemists who took up work with diethyl azodicarboxylate soon adopted for this ester the acronym "DAD."²¹ In 1972, William Hoffman, a student in Professor Bose's laboratory, somehow felt this term was disrespectful of fathers, so he expanded the alphabet to "DEADC." (Those days the Dead Sea scrolls were often in the news.)²¹ Some years later Dr. Bose met Jan Sjövall at a World Health Organization conference in Stockholm and learned that Sjövall's co-





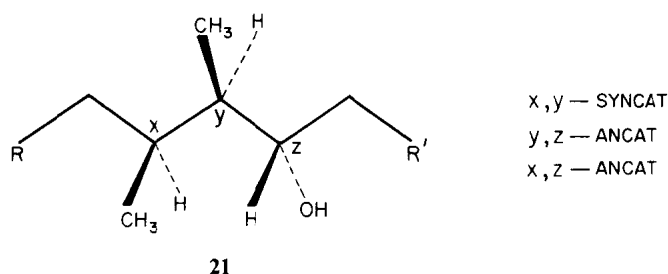
workers Josef Herz and Thomas Baillie at the Karolinska Institute had their own abbreviation for the Mitsunobu process: “DEADCAT.” Its origin is not quite as suggested in the literature²² but is *diethyl azodicarboxylate; acid; triphenylphosphine*.^{23–25} Amused by this acronym, Bose’s bunch adopted and shared it with Frank DiNinno at Merck, Sharp and Dohme Laboratories, who included it in a paper in the *Journal of the American Chemical Society*.^{26,27} Shortly thereafter, cartoonist Simon Bond hit the lay world with his picture-book, *101 Uses for a Dead Cat*.²⁸ Mr. Bond is not a chemist, so the events are quite unrelated. But his feline caricatures did not sit well with many cat lovers and may have contributed to chemists favoring the shorter acronym “DEAD”²⁹ or “DEADC”³⁰ in publications dealing with diethyl azodicarboxylate. Indeed, when Professor Bose submitted a communication to the *Journal of Organic Chemistry* he was informed that DEAD was the preferred shorthand.²¹ Going one step further, he termed the reaction “DEAD-TPP” and so gave equal status to triphenylphosphine, the other necessary reagent.³¹ Dr. DiNinno would have opted for “DEAD-TRIPP,” except that it sounded rather foreboding.²⁷ Incidentally, his colleague R.P. Volante at Merck, Sharp and Dohme found it experimentally advantageous to replace DEAD with *diisopropyl azodicarboxylate* in some applications of the Mitsunobu reaction.³² This latter reagent has been dubbed “DIAD.”³³ (But don’t use it for diadic tautomerism, chapter 14.) Although the nickname DIAD seems simple enough, we wonder what onomastic evolution lies in store. Charles Darwin would have wondered too.

By the way, feline fans, although cats were dropped from DEAD methodology, they found secure perches elsewhere. For example, your hospital may have access to a CAT scanner (computerized axial tomography) for medical diagnoses. It’s not cute, but you couldn’t find anything nicer for a PET (positron emission tomography).³⁴

Louis and Mary Fieser, renowned chemists, educators, and writers, loved Siamese cats and even graced their books with pictures of these regal animals. So you might think that when the Fiesers coined the term “cathylate,”³⁵ its first three letters meant another plug for the feline species. Actually, however, the word is but a contraction of carboethoxylate. Research in their laboratory had revealed that ethyl chlorocarbonate (dubbed “cathyl chloride”)³⁵ selectively carboethoxylates equatorial secondary alcohols and not axial ones, so “cathylation” proved useful in chemical manipulation of polyhydroxysteroids.³⁶

Nonetheless, cats do know their stereochemistry, thanks to Francis Carey of the University of Virginia and Martin Kuehne of the University of Vermont. These chemists coined “syncat” and “ancat” to specify relative chirality at sites in acyclic molecules.³⁷ For example, in an extended staggered (zig-zag) chain, two centers are

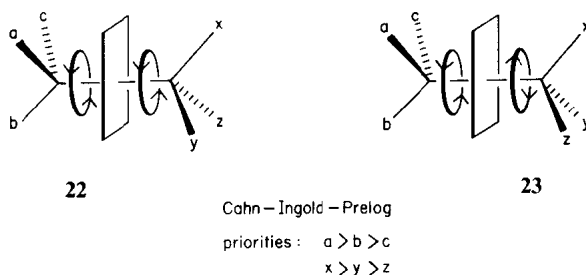
“relative syncat” when they dispose their larger substituents on the same side of the planar chain; in “relative ancat” these groups project to opposite sides. Structure **21** shows a simple case, where *x*, *y*, and *z* would be replaced by the appropriate carbon

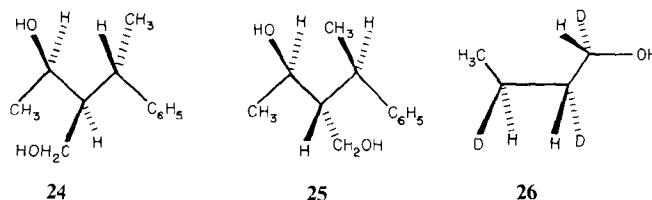


numbers. Syncat and ancat are merely contractions of syn-catenoid and anti-catenoid (*catena* is Latin for “chain”). We are glad Professors Carey and Kuehne eschewed “anticat”; otherwise purrs might have epimerized to growls.

Configurational description based on substituent “size” serves well in many circumstances. But for rigorous identification of relative chirality these same researchers coined the descriptors “priority reflective” and “priority antireflective.” Their respective acronyms are “pref” and “parf”; and priority refers to sequence-rule priority according to the Cahn–Ingold–Prelog convention.³⁸ In the Carey–Kuehne terminology, two contiguous chiral centers have a pref relationship if the order of decreasing priority of the three remaining substituents at one center is a mirror reflection of the order of decreasing priority of the groups at the other center (e.g., **22**). When two descending-order circuits lack reflection symmetry, the relative configuration is parf (e.g., **23**). Such designations of relative stereochemistry are independent of conformation because they compare priority-determined *order*, and not momentary *spatial positions*, of the substituents. This system obviates the well-known ambiguities associated with terms like threo and erythro and can accommodate structures with nonadjacent, or with multiple, chiral centers. In the latter case, you need only identify them with numbers and treat each pair of centers independently of all others. For example, of the four diastereomers of 3-(hydroxymethyl)-4-phenyl-2-pentanol, structure **24** is the 2,3-*parf*-3,4-*pref* isomer; and **25** is 2,3-*pref*-3,4-*pref*. And what about the trideuteriobutanol **26**? Parf–parf!

If you are not completely happy with syncat/ancat and *pref*/*parf*, try out a stereochemical notation developed by savants Dieter Seebach and Vladimir Prelog, at the ETH in Zurich. Whether you fancy reactants or products, the Seebach–Prelog notation for the steric course of asymmetric syntheses has much for you to “like” and “unlike,” and employs the symbols *lk*, *l*; *ul*, *u*.^{39a} Earlier, Ivar Ugi had recommended a system that used the descriptors *p* and *n*.^{39b}





By now you may think that the feline family does well by chemists. Quite right. But cats fare even better in physics, where they have appeared as authors on research papers. In 1975, Professor Jack H. Hetherington (Michigan State University) wrote a theoretical paper on his own and was about to send it to *Physical Review Letters*.⁴⁰ But a colleague warned that the manuscript would be returned because of an editor's rule that words like "we" and "our" should not be used in a publication with only one author. Dr. Hetherington did not relish revising and retyping the whole text, so, instead, he simply added a co-author: his Siamese cat Chester (sired by Willard). And for legitimacy, he tacked on two more initials, FD (from *Felix domesticus*), to create "F.D.C. Willard." The Hetherington–Willard article was duly published⁴¹; and Mrs. Hetherington went on sleeping with both authors.

Eventually, the cat had to be let out of the bag when a visitor came to campus to see Professor Hetherington, found him unavailable, and then asked to speak to Willard. The feline caper also unfolded internationally when J.H.H. mailed reprints to a few friends. The usual annotation "Compliments of the authors" included his signature and an imprint of pussy's inked paw!^{41,42}

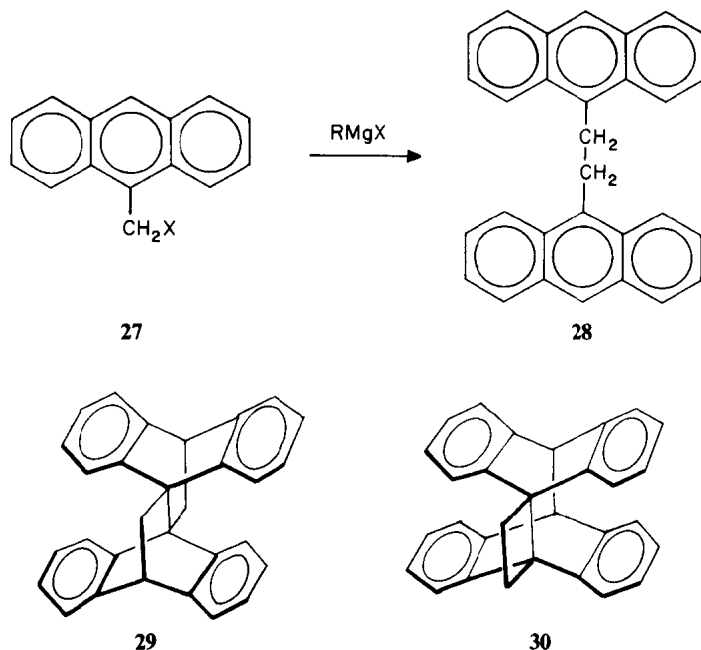
Willard became bilingual and authored his second paper in 1980 in *La Recherche*.⁴³ This French article about antiferromagnetism in solid ³He was intended for broad readership and was put together by a group of French and American physicists, including Professor Hetherington. But, because of some disagreement about its content, F.D.C. Willard ended up as the sole author. That way, if the paper had flaws, the cat could take the rap.⁴⁰ Occasionally one sees references to "F.D.C. Willard, private communication." And sometimes in acknowledgments he is thanked for "helpful discussions."⁴⁰ Although F.D.C.W.'s future in physics is uncertain, we like his style and hope he gets tenure.

In the field of chemistry, the American Chemical Society has virtually squelched any hope for mischief along "authorship" lines. Its "Ethical Guidelines to Publication of Chemical Research" establish criteria for co-authorship and stipulate that "no fictitious name should be listed as an author or co-author."⁴⁴ But we wonder whether co-authorship would be sanctioned for a cat that performs some of the laboratory work? An unlikely scenario you say? Perhaps unlikely in chemistry, but not in physics. In fact, Johns Hopkins physicist Robert W. Wood, an inventive genius and one of the founding fathers of spectroscopy, called upon feline help to clean out a spectroscopy tube he had built in a barn.⁴⁵ The wooden tunnel, 42 feet long and about 6 inches wide, projected outside the barn and accumulated cobwebs when not in use. Professor Wood popped the family cat in at one end of the shaft. Pussy squirmed through and thus swept the passage free of cobwebs. In 1912, Dr. Wood reported his cleaning method in *Philosophical Magazine* but did not name his feline assistant.⁴⁶

The notion to conscript four-legged friends into laboratory service took hold. Around 1970, scientists at the Atomic Energy Commission's National Acceleration Laboratory, Batavia, Illinois, used a ferret, named Felicia, to clean long synchrotron tubes. The NAL engineers had originally planned to build an expensive pipe cleaner; instead, they bought Felicia for \$35, fitted her with a harness, and let her drag cleaning

cloths through the 300 ft tubular sections.⁴⁷ And telephone and electric companies were known to train, induce, or seduce small animals to scamper through long pipes dragging wires behind them.⁴⁸ But enough of this; let us return to chemistry and look to molecules for divertissement.

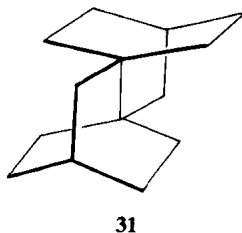
The coupled compound 1,2-bis(9'-anthranyl)ethane (**28**) can be prepared from 9-(halogenomethyl)anthracenes (**27**) with Grignard reagents.⁴⁹ One or two side products



turn up, and early workers disagreed about their structures.^{50–53} Henri Bouas-Laurent at the University of Bordeaux cleared up the controversy in 1975.⁵⁴ Evidently, when the reaction is conducted in the dark, the side product is **29**. But in light, some of the main product, **28**, isomerizes to **30**; so both side products may be present in the mixture. Ultimately, X-ray crystallography proved the constitution of **29**.⁵⁵ Interestingly, structure **29** had been proposed in a thesis at the University of Minnesota in 1962, but it was not published in a journal.⁵⁶

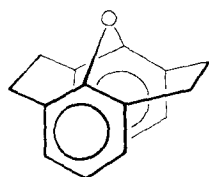
Understandably, these formulas filliped the imagination of Dr. Bouas-Laurent. The phenylene rings reminded him of wings. In **29**, each pair of wings is displaced from the other, as in a butterfly; so he called it “lepidopterene.” (*Lepidoptera* is the order of insects consisting of butterflies and moths; it comes from Latin *lepis* (“scale”) and Greek *pteron* (“wing”).) On the other hand, in **30** the wings are superposed, just as in a biplane of World War I vintage. Hence, the name “biplanene” took to the air.⁵⁷

Other syntheses of lepidopterene have been published.^{58,59} Also, a lepidopterene-like molecule with clipped wings (**31**) was prepared at The Ohio State University by Leo



Paquette's group, who named it [2, 2, 2] "geminane" (see p. 179)⁶⁰; it consists of two equal parts, and the Latin *geminus* means "twin."

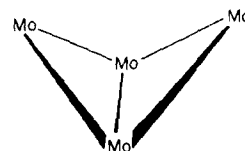
While on the subject of butterflies, we note that the term "butterfly" also was applied, by Arnold Gordon and John Gallagher of The Catholic University of America, to the *syn* conformation of certain metacyclophanes such as **32**.⁶¹ The oxygen bridge keeps the "butterfly" from becoming a "ladder" (**33**, the *anti* conformation⁶²). Talk about metamorphosis! Inorganic complexes have enhanced the beauty and diversity of butterfly collections. For example, researchers in Milan, Italy, bagged an iron "butterfly" cluster.⁶³ And Malcolm Chisholm's coterie at Indiana University showed that the molybdenum atoms in solid $\text{Mo}_4\text{Br}_4(\text{O}i\text{Pr})_8$ place themselves as in **34**.⁶⁴ And you may come across an ephemeral "butterfly" if Robert Bach's bunch at Wayne State University can induce you to probe the mechanisms of alkene oxidation by peroxy acids.⁶⁵



32



33

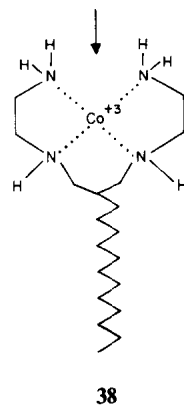
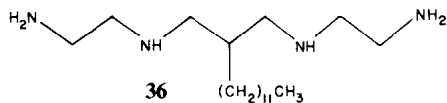
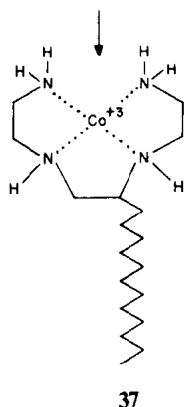
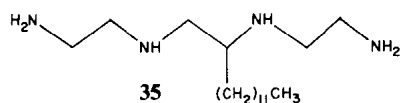


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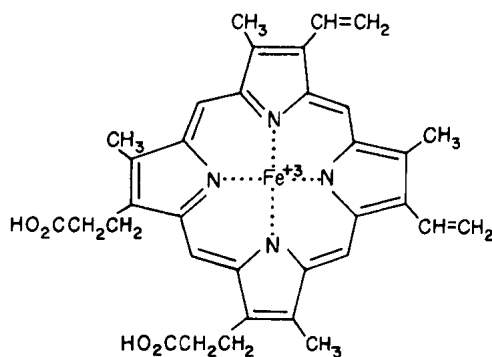
Even the lowly earthworm has inspired chemists. Jacques Simon and co-workers at Centre de Recherches sur les Macromolécules, Strasbourg, found that **35** and **36** bind nicely with transition metal ions such as Co^{+3} to give complexes **37** and **38**, respectively.⁶⁶ Molecular models of these complexes reminded Dr. Simon of a washer-like ring, with a ball stuck in the hole and an earthworm dangling off the edge (see **39**). The "ball" is, of course, the metal ion. Because earthworms belong to the phylum of invertebrates known as Annelida, Dr. Simon adopted "annelides" for this class of compounds. As luck would have it, archaic French for "ring" is *anel* (derived in turn from the Latin word for ring, *anulus*; diminutive form, *annelus*).^{*} Thus, the name

^{*}The Latin *anulus* is sometimes spelled "annulus," and chemists use terms such as "annellation" or "annulation" for the synthetic process of building a ring onto a molecule. In an article titled "A Review of Annulation," UCLA's Michael Jung favored the "u" over the "e" spelling in accord with the dictionary preference.⁶⁷ However, Paul Caluwe at the State University of New York (Syracuse) took the opposite stance in his review titled "Heteroannelations with *o*-Aminoaldehydes."⁶⁸ Chemists seem to be divided on this "trivial" issue, and both spellings are common. Perhaps we should defer to the first use of the term in the organic chemical literature. A German article in 1919 by Polish researchers Wl. Baczyński and St. von Niementowski contains the phrase "durch lineare Anellierung der Ringe."⁶⁹ (Do you know of an earlier use?) However, Matthew Schlecht (Polytechnic Institute of New York) informed us that annellation (also spelled anellation and annelation) has appeared in contexts other than that of Baczyński and Niementowski's "ring-forming reactions."⁷⁰ For example, in 1932 Eric Clar described multicyclic aromatic systems as being related to simpler ones by linear or angular "anellation" (Anellierung), in other words, by formal ring addition.⁷¹ And Jerry March's textbook *Advanced Organic Chemistry*⁷² taught annellation as the "phenomenon, whereby some rings in fused systems give up part of their aromaticity to adjacent rings." So, avers Professor Schlecht, the term is thus rendered ambiguous, because it can mean "ring-forming reaction," a "ring-added relationship," or "aromatic ring character partitioning." In contrast, annulation has no meaning other than the formation of rings, and the spelling is more constant. Finally, for chronological record, Dr. Schlecht pointed out that the first principal chemical usage of the term annellation in English was by William S. Johnson and co-workers in a 1960 paper titled "The Nature of the Intermediary Ketols in the Robinson Annulation Reaction."⁷³ And annulation showed up initially in a 1970 communication by Elias Corey and Joel Shulman with the heading "A Method for the Introduction of Two Carbon Appendages at a Carbonyl Carbon. Application to Double Chain Branching and Spiro Annulation Operations."⁷⁴ The following year, Charles Scanio and Richmond Starrett titled a publication "A Remarkably Stereoselective Robinson Annulation Reaction."⁷⁵ Unless IUPAC or the like⁷⁶ deigns to proclaim a preference, annulation/annellation may remain a dichotomy in chemistry writing.

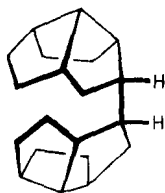
“annelides” actually embraces both the worm and the ring parts of these interesting molecules.⁷⁷



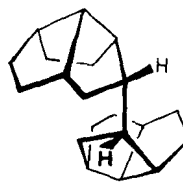
Because annelides sport polar heads and nonpolar tails, they are surfactants and tend to form “supramolecular structures” in which the polar tips of many molecules attract one another.⁶⁶ Such aggregates are also called micelles. Furthermore, the polar end with its encumbered ion is somewhat akin to a porphyrin-Fe complex, as in the heme portion of hemoglobin (**40**). And, not surprisingly, annelides **37** and **38** can bind molecular oxygen.⁶⁶



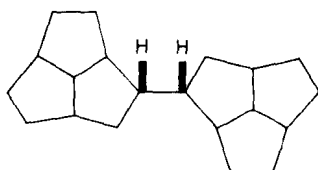
Some aquatic species became immortalized by chemical names. Molecular models of compounds **41** and **42**, which Professor Leo Paquette and his co-workers synthesized in 1975,⁷⁸ reminded them of an open clam, or oyster, shell. Hence, they dubbed these structures “bivalvanes.” Interestingly, **41** and **42** are DL and *meso* diastereomers. You can appreciate this structural difference better from the flattened formulas, **43** and **44**.



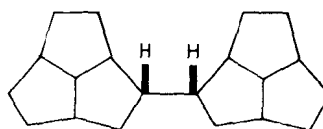
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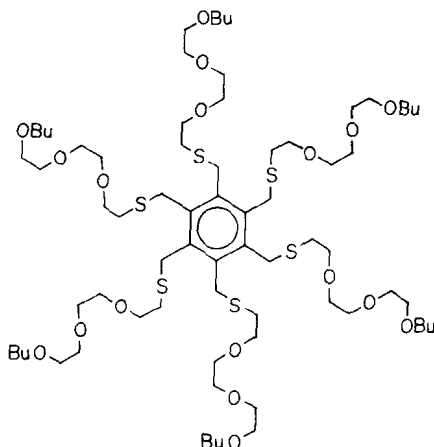
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44

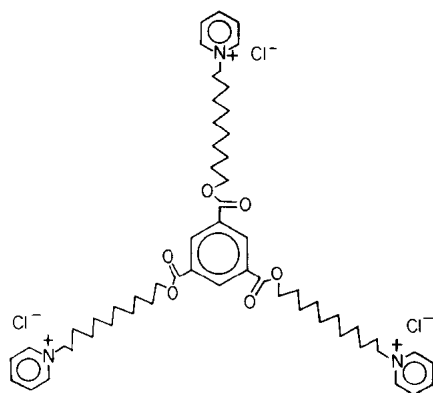
Dr. Paquette wanted to synthesize **41** because mental joining of the two halfshells by five more carbon-carbon bonds produces the fascinating dodecahedrane (**1**). His team first developed routes to the halfshells and then hooked them together by a pinacol-type reduction.⁷⁹ Removal of the hydroxyl groups left Dr. Paquette's beachcombers ready for their clambake.

Chemists Fritz Vögtle and Edwin Weber, then at the University of Würzburg, have constructed molecules such as **45**.⁸⁰ As Dr. Vögtle is a compressed-air diver and an avid reader about marine life, it is not surprising that he called them "octopus molecules."⁸¹ The word "octopus" comes from Greek *okto-* (eight) and *pous* (foot). Actually his

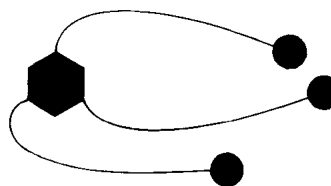


45

compounds own but six tentacles and might have been christened "hexapus." In any case, Dr. Vögtle's term is apt because the heteroatoms act like the suction cups with which a real octopus grasps food. For compound **45**, the meal consists of metallic ions, which the sulfur and oxygen donor atoms envelop with great tenacity. Its appetite for ions from main groups I and II of the periodic table⁸² is more voracious than that of known crown ethers (chapter 2) and about the same as that of cryptates (chapter 17). A molecular octopus with shorter tentacles doesn't grasp ions as tightly. Hunger also wanes when you replace the oxygen suction cups by CH_2 groups.



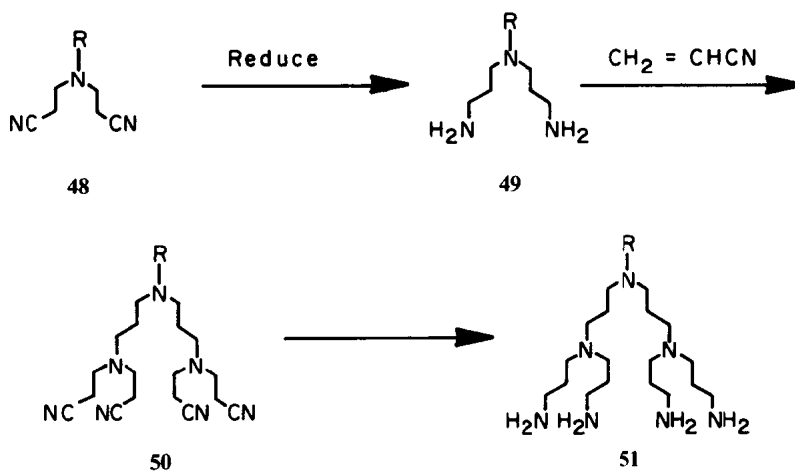
46



47

Since the appearance of the first octopus molecule, other species have invaded the chemical aquarium, including molecules with different types of bodies and tentacles.^{83,84} The numerically more accurate term “hexapus” for molecules with six tentacles has appeared in print, thanks to Fred Menger of Emory University, who also contributed other hydronyms* (p. 121).⁸⁵ And Colin Suckling of the University of Strathclyde, Glasgow, thought that three tentacles may be enough to do a job. For example, he found that **46** forms complexes with small aromatic substrates, and can thereby influence their reactivity (e.g., **46** inhibits the chlorination of phenol.) Professor Suckling referred to **46** as a “tentacle molecule,” in other words, a detergent-like molecule whose motion is restricted by attachment to a central framework (see **47**).⁸⁶ But you may call it triapus. Or even trigapus.⁸⁷

If you like tentacles and need lots of them in a hurry, Professor Vögtle and colleagues at the University of Bonn advocate their principle of “cascade” synthesis.⁸⁸ In this approach, they manipulate a functionalized molecule to get a product armed with twice as many of those same functional groups. Then, repeat the manipulations and you again double the units. For example, bis(cyanoethylation) of RNH_2 gave dinitrile **48**, reduction of which afforded the bitentacled amine **49**. Carried through once more, the process converted this compound to **50** and then to **51**. Such heavily armed structures might be good ligands for grasping ions.



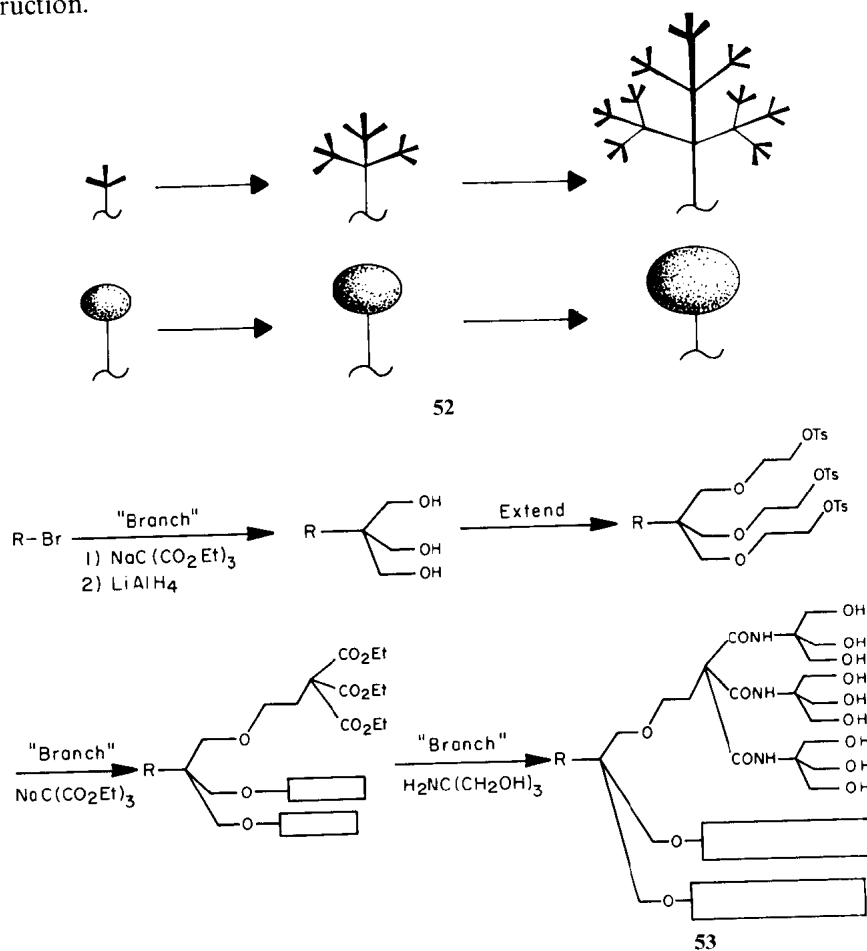
*A hydronym is a name of a body of water. We are stretching the term to include other aqueous items.

The reagent used for these cyanoethylations was $\text{CH}_2=\text{CHCN}$. If you ever need a large quantity of this chemical and want delivery without delay, it might be prudent to specify acrylonitrile rather than vinyl cyanide. A story recounted in *Chemical and Engineering News* tells us why.⁸⁹

It seems that in the early days of the U.S. synthetic rubber industry a company ordered an 8000 gal tank car of vinyl cyanide for use as a copolymer with butadiene to produce an oil-resistant rubber. The Interstate Commerce Commission refused permission to ship the chemical by rail on the grounds that cyanides are poisonous. What would happen in the event of an accident? How would the public react to ICC's allowing a volatile cyanide to be transported by rail?

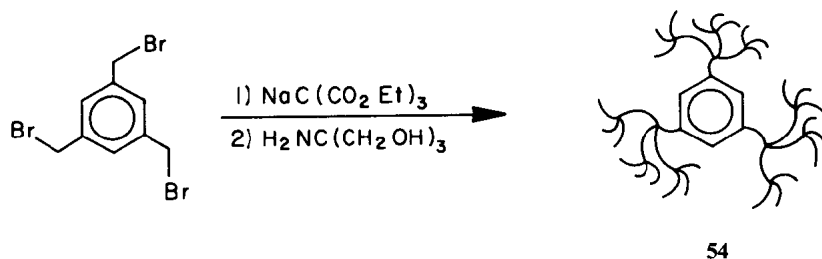
The impasse was broken by a minor chemist in the company, who suggested that an order be placed for a tank car of acrylonitrile. The company did so, and the chemical was delivered without objection from the ICC. The minor chemist later became an executive.⁸⁹

The essence of cascade synthesis is progressive branching. Branches bring to mind trees, and that's just how George Newkome (then at Louisiana State University) and his colleagues got into new cascade approaches to unusual micellar structures. Their concept was based on an architectural model of trees (called the Leeuwenberg model), and they applied it to synthesize a highly branched prototype with an outer surface of polar groups.⁹⁰ Drawing 52 pictorializes this model as applied to micellar construction.

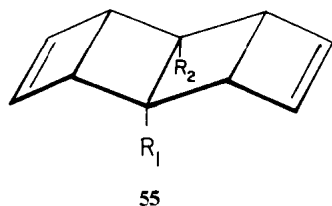


Specifically, Newkome and his rangers prepared **53** by a three-tiered construction sequence as shown. This multitendrilled monster turned out to be miscible with water despite its high molecular weight (> 1600). Because this unidirectional cascade is based on arboreal design (Latin *arbor* means “tree”), Professor Newkome and co-workers termed their products “arborols.” Structure **53**, has 27 branches, so that makes it a [27]-arborol. (Tomalia *et al.* independently described a similar class of cascades termed “starburst-dendritic” polymers.⁹¹ In Greek, *dendro* means “tree.”) Professor Newkome likened a Leeuwenberg cascade in two directions to a tree with its accompanying root system,^{90b} and he named these “sylvanols” (*silva* is Latin for “forest”).⁹⁰

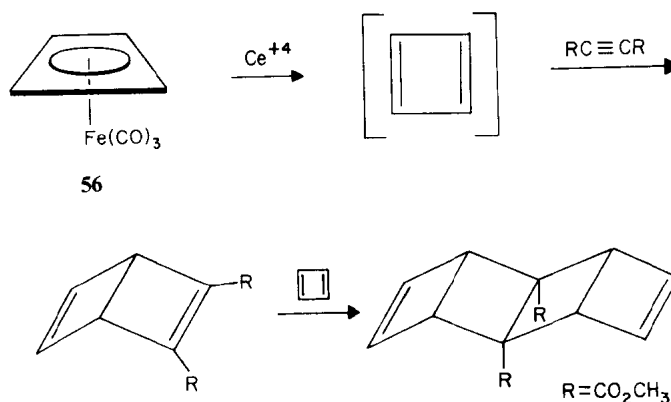
The Louisiana State researchers also extended their chemistry to three directions by synthesizing **54**, in which a trio of cascades emanate from a benzene core. Light-scattering experiments indicated that aggregates of **54** in solution have micellar character.⁹²



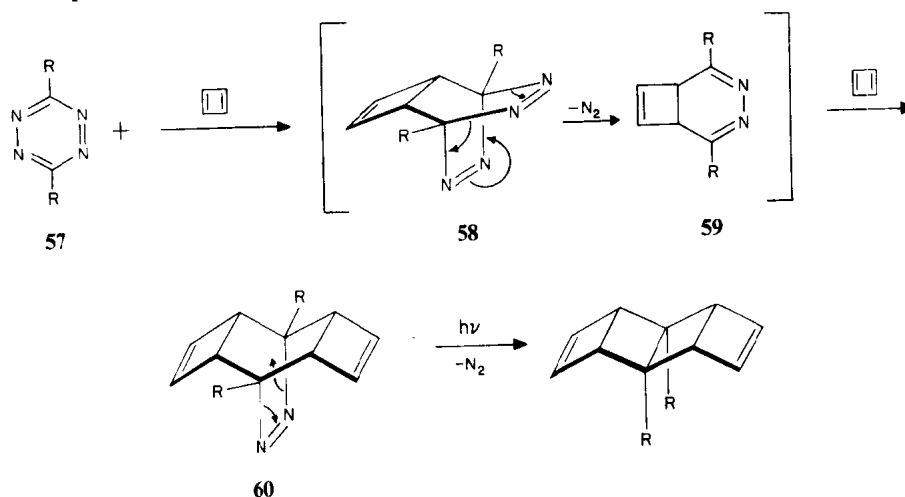
Animals that inspire names are not always found in trees, zoos, or oceans—at least not in our times. Consider compounds **55**, which their creator, Rowland Pettit of the University of Texas at Austin, dubbed “pterodactyladienes.”^{93,94} These structures reminded him of the extinct flying reptiles known as pterodactyli. This word is Latin, but stems from the Greek *pteron* (wing) and *daktylos* (finger). Such creatures had winged membranes extending from the side of the body to the end of the greatly enlarged fourth digit (“finger”). Professor Pettit and co-workers synthesized their



prehistoric creatures from cyclobutadiene, a molecule whose own existence was questioned for many years. When cyclobutadiene is released from its iron tricarbonyl complex (**56**) in the presence of ceric ions and a suitable alkyne, two successive cycloadditions generate the pterodactyladiene. Each cyclobutadiene ends up as a wing tip. If these cycloadditions are $[4 + 2]$, then Drs. Diels and Alder could be considered godfathers of Professor Pettit's prehistoric offspring.

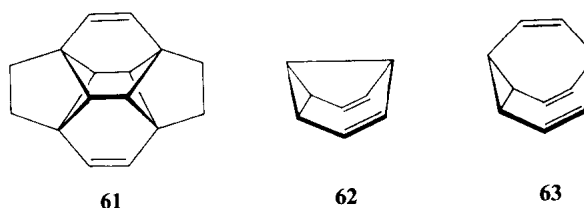


Hans-Dieter Martin and Mirko Hekman at the University of Würzburg increased our knowledge of these winged molecules. They prepared pterodactyladienes with several other R groups (“heads” and “tails”)^{95,96} and also hydrogenated the double bonds to produce the parent pterodactylanes.⁹⁷ In their intriguing synthetic variation,



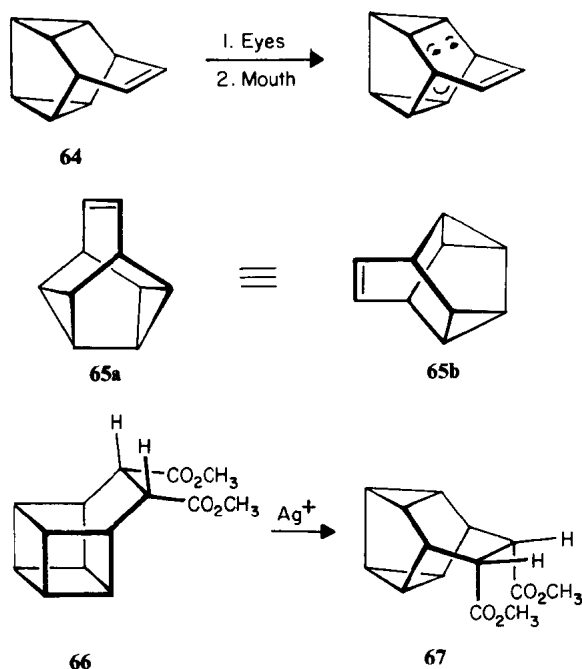
cyclobutadiene takes the opposite role in a Diels–Alder merger with **57**. Adduct **58** plays the organic chemist’s favorite game, electron reorganization, to **59**. Another $[4 + 2]$ cycloaddition gives **60**, a pterodactylus with a pot belly of two nitrogens. Then, a dash of UV light, more electron scrambling, and (voilà) the belly is gone. Weight watchers take note! Professor Martin continued his chemical ornithology at the University of Düsseldorf, where, in 1981, he and his colleagues worked out still another posthistoric route to this prehistoric bird.⁹⁸

You might think that the titles “equinene” for **61** and “calfene” for **62** belong in our discussion of animal shapes. However, equinene was named after a two-legged “horse” rather than a four-legged one. And calfene (so labeled by Maynard Sherwin, a graduate

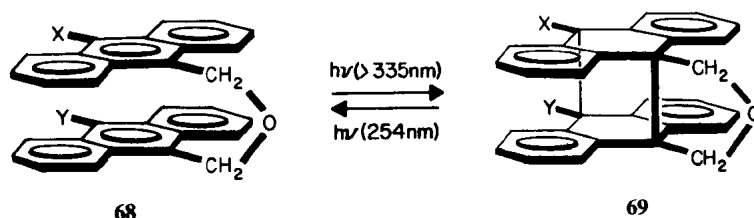


student of Howard Zimmerman, in whose Wisconsin laboratory it was synthesized⁹⁹) got its tongue-in-cheek name from the fact that it is an incompletely grown bullvalene (**63**) (i.e., it lacks one ethyleno bridge). More conservatively, the chemical literature usually refers to **62** as "semibullvalene." Interestingly, the story of bullvalene itself involves a two-legged creature; we discuss it along with equinene in chapter 10.

How about naming a molecule after a part of an animal? Professor Paquette has done just that with **64**, which he dubbed "snoutene."¹⁰⁰ This onomastic oddity was inspired by the realization that **64** can be made to look like Pinocchio (the young lad in the classic children's story whose nose grew each time he told a lie.) The flattened "nose" also reminded Paquette of a crocodile snout; and when you look at **64** from different directions it even resembles a maybasket (**65a**) and a large scoop (**65b**). Hence, the Ohio State University researchers also considered "maybasketene" and "large scoupe"; but "snoutene" finally won by a nose.¹⁰¹ A key step in the synthesis of snoutene was rearrangement of **66** to **67**, a remarkable silver-ion-catalyzed skeletal change reported by Paquette¹⁰² and by Dauben.¹⁰³

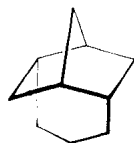


The photic interconversion of molecules **68** and **69** struck Henri Bouas-Laurent and co-workers at the University of Bordeaux as being similar to the closing and opening of a jaw.¹⁰⁴ Compounds **68** are yellow and **69** are colorless, so irradiation brings about a color change (photochromic). This last term comes from the Greek *phos* (light) and *chroma* (color). Therefore, Professor Bouas-Laurent called their system "jaw photochromic."¹⁰⁴ The jaw closure is a photochemically allowed $[4 + 4]$ cycloaddition,

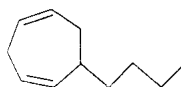


suprafacial in both components; jaw opening is just the reverse. Furthermore, the closure occurs at wavelengths > 335 nm (i.e., with light absorbed by the yellow reactant but not by the colorless product). To force the jaw to open, inject light that is absorbed by **69**; and 254 nm “fills the bill” perfectly. We’re dealing with a very intelligent jaw.

The name “cristane,” bequeathed to tricyclo[5.3.0.0^{3,9}]decane (**70**),¹⁰⁵ emerges from an animal part but not because of the molecule’s shape. Langley Spurlock of Brown University, originator of cristane, put the matter most delicately.¹⁰⁶ The word derives from “crissum,” the area around the cloacal opening under a bird’s tail. It happened that on the evening the compound was chemically identified someone left a laboratory window open. During the night one of the pigeons frequenting the window ledge got into the room and apparently spent much time trying to find its way out. Next morning the laboratory benches and floor were covered with unwelcome evidences of the bird’s anxiety while it had attempted to escape. Spurlock’s clean-up crew, therefore, named their new tricyclic molecule in honor of the bird’s anatomical region that provided the “surprisingly abundant gift.” We salute the Spurlock team for coining a name for posterity.



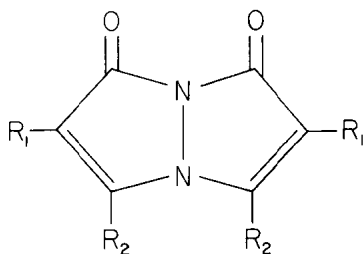
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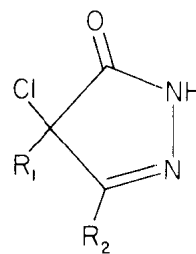
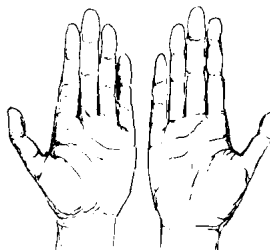
71

We may stretch things a bit to refer to sperm as a part of an animal, but not if we think of the very beginning of the animal’s existence. In any case, when Subramania Ranganathan of the Indian Institute of Technology of Kanpur noted structure **71** (a constituent of an essential oil of algae of the genus *Dictyopteris* and hence also known as dictyopterin C’ in the literature¹⁰⁷), he jokingly dubbed it “spermane.”¹⁰⁸ This molecule possesses a “head” and hydrocarbon “tail,” just like the annelides we described earlier. Obviously, the title given a compound is based on what is in the mind of its beholder.

The name “bimanes,” derived from the Latin *bi* (two) and *manus* (hand), was assigned to molecules with structure **72** by their inventor, Edward Kosower, because they resembled two hands.¹⁰⁹ These compounds arise from **73** by the action of base. After



72



73

looking at the clever mechanism Professor Kosower proposed for this reaction, you will undoubtedly want to give him a hand, or perhaps even two (one for each of his two academic homes: Tel Aviv University and the State University of New York at Stony Brook).