

*HANDBOOK OF*  
**HYDROCARBONS**

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# HANDBOOK OF HYDROCARBONS

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科學院圖書



## PREFACE

Uses of hydrocarbons have rapidly expanded in both volume and variety, and there have been correspondingly rapid additions to the number whose properties are known. Some of these new compounds have been recovered from natural or manufactured mixtures, while others have been directly synthesized. For still others, which have never been examined in pure state, their properties have been "synthesized" by brilliant and painstaking work in correlating the known properties of closely related compounds.

Indeed, the number of reported hydrocarbons has become so large that, with the customary arrangement of tables, it is often difficult to locate a given compound, or even to be sure whether or not it is listed. If one has a hydrocarbon of unknown identity but known boiling point, it is a long search to find clues.

It has been the purpose of this work to prepare tables giving the most important physical properties of all hydrocarbons whose boiling points have been recorded, in such form that

1. All compounds boiling at or near a given value are listed together.
2. A specific hydrocarbon can be promptly located.

These ends can be best accomplished by listing each hydrocarbon in each of two tables. The order in Table A is that of the boiling points at 760 mm Hg, and other properties are also given. In Table B, the compounds are in groups of the same empirical formula and same type (as defined in the Introduction) and are arranged within groups alphabetically by parent compound. The boiling point of each compound is given, so keying it back to Table A.

Table C lists alternate names, including common and trivial names, and Table D gives the numbering of representative cyclic hydrocarbons.

The Handbook should offer real help to any investigator who wishes either to locate the properties of a specific hydrocarbon, or to obtain a quick summary of the indications which the literature affords as to what compounds may be present in a cut of known boiling point or range.

Such investigators should include academic, institutional, government and industrial workers, not only in the predominantly hydrocarbon fields such as petroleum, natural gas, shale oil, coal and rubber, but also in the chemical, "petrochemical," and plastics fields.

S. W. FERRIS

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## INTRODUCTION

It was in 1842 that Schiel called attention to the phenomenon of homology, giving as evidence the alcohol radicals. Shortly thereafter Dumas noted it in the fatty acids, but the hydrocarbon series soon became the favorite examples.

The value of Schiel's contribution to the study of hydrocarbons was tremendous, but it has led to a hardship for many workers in one respect, namely, the tendency to group hydrocarbons by homologous series when compiling properties.

Suppose, for example, that a hydrocarbon has been synthesized and carefully fractionated, or that one has been recovered from a natural mixture, and that the presence of impurities is suspected. The worker would like to know what other hydrocarbons might be present, and knowing the approximate boiling point he repairs to compilations. He must, however, search scores of tables to find a few compounds with boiling points close to that of the preparation.

A similar situation develops when an unexpected flat is found on the chart of a fractional distillation. In either case it requires a literature search of the first magnitude before the investigator can feel that he has turned up even a reasonable majority of the known compounds which may be lurking in his sample.

### Table A

If hydrocarbons were listed in the order of their boiling points, the extended survey of the literature would be replaced by a few minutes of examination. Table A contains the hydrocarbons whose boiling points have been recorded up to the early part of 1954. It represents an attempt by the present compiler to do, for the full range of hydrocarbons, what many have been forced to do for the restricted ranges in which they were interested.

Boiling points are recorded in the literature at a bewildering variety of pressures. All values have been corrected to 760 mm, by methods which will be discussed later.

### Table B

If, however, one wishes to find the properties of a specific hydrocarbon, Table A becomes hopelessly inadequate. Alphabetical listing is also unsatisfactory, first because of differences in systems of nomenclature, and secondly because different parent compounds may be correctly chosen in naming a given compound, even with the same nomenclature system. It would at first

appear that listing by homologous series now becomes the proper method, but reflection shows that not to be the case, for the reason that no two people could be expected to agree upon how to group the several thousand compounds already described, to say nothing of the many thousands which will eventually be reported. This situation arises from the fact that there are too many variations, particularly if monoolefins are to be separated from di-, tri-, and tetraolefins, and if acyclic compounds containing both double and triple bonds are to be compartmented from those which have only triple bonds. With molecules containing both aromatic and non-aromatic rings, with double or triple bonds in the side chains, or perhaps with the chains attached to the rings by double bonds, individuals can hardly be expected to agree as to how they should be classified. Accordingly, it is difficult to find a complex hydrocarbon in a compilation broken up into tables of homologous or similar compounds.

Searching is much easier in the formula index of *Chemical Abstracts*. If the empirical formula is known, a list can immediately be found which will include the compound in question if CA has reported upon it. Such lists in the annual indexes are of modest length. In a decennial index they may be long enough to require considerable time, since one must proceed slowly enough to be sure that the wanted compound is not masquerading under a different name. A list of all recorded hydrocarbons of a given empirical formula is sometimes discouragingly long.

A further breakdown therefore becomes desirable, but it should be sufficiently specific that all concerned can agree upon the group in which any hydrocarbon belongs. Such a breakdown is readily available, based on the seven types of carbon-to-carbon linkage, namely, single, double, and triple bonds in acyclic structures, single, double, and triple bonds in cyclic structures, and finally rings containing single and double bonds, fully conjugated.

If a molecule is to be examined to note how many of these linkage types are present, and in what combinations, uncertainties remain, but if agreement can be had on an order of "peculiarity," then the molecule may be examined only for the "highest" order, and classified accordingly. That order seems apparent, and is the one given above, with acyclic single bonds being the most commonplace, and the aromatic ring the most distinguished.

Names too are ready at hand, so that the seven types are:

Type	Characteristic C—C Linkage
Alkanes	Single bonds in acyclic structures
Alkenes	One or more double bonds in acyclic structures
Alkynes	One or more triple bonds in acyclic structures
Cyclanes	Single bonds in cyclic structures
Cyclenes	One or more double bonds in cyclic structures
Cyclynes	One or more triple bonds in cyclic structures
Aromatics	One or more aromatic (fully conjugated) rings

As indicated above, the alkanes are considered the "lowest order" of hydrocarbons, and the aromatics the "highest order." Each hydrocarbon is assigned to the highest possible order.

Table B arranges hydrocarbons in groups of the same empirical formula, and the same type, as defined above. If either a systematic name or the structural formula of a compound is known, it is immediately apparent to which of the seven types it belongs, and when the empirical formula is known it is the work of a moment or two to determine whether it is included in Table B.

### Table C

Finally, there is the problem of locating a compound when the name by which it is known to the investigator is different from that used by the compiler, particularly when the known name does not reveal the structure. Many such names are called trivial, a term which, if not used in a faintly derogatory sense, usually means non-systematic. There are certain good uses for names which can be pronounced in a single breath, and Dr. Crane has well pointed out that both methane and benzene are trivial names.

Table C lists alternate names alphabetically, together with the names used in the Handbook, and the subdivision of Table B where each compound may be found.

### Table D

An alphabetical listing of the numbered formulas of various hydrocarbons is given in Table D.

### Nomenclature

What follows does not purport to be a complete discussion of the vexing subject of nomenclature, but rather a statement of the methods employed, together with brief reasons for choosing one over another.

If one has even a modicum of originality, it is quite impossible to work with thousands of systematic names without occasionally wondering whether the system couldn't be improved here or there. It was early decided, however, to sternly repress any such tendencies. The two reasons for that decision were that a tremendous amount of excellent thinking has already been devoted to the problem, and there are already too many different systems in use.

The four references which follow this discussion, together with ring systems employed in recent *Chemical Abstracts* Subject Indexes, were used as the basis for consideration. Whenever agreement was found between the International Union of Pure and Applied Chemistry and *Chemical Abstracts*, those features were adopted, even though the compiler disliked a few of them. Where disagreement was found, that one was chosen which seemed



most logical, with perhaps a little leaning toward *Chemical Abstracts* in resolving doubtful cases.

The names of the *straight-chain alkanes* follow.

Number of Carbon Atoms		Number of Carbon Atoms	
1	Methane	19	Nonadecane
2	Ethane	20	Eicosane
3	Propane	21	Heneicosane
4	Butane	22	Docosane
5	Pentane	23	Tricosane
6	Hexane	24	Tetracosane
7	Heptane	25	Pentacosane
8	Octane	26	Hexacosane
9	Nonane	27	Heptacosane
10	Decane	28	Octacosane
11	Undecane	29	Nonacosane
12	Dodecane	30	triacontane
13	Tridecane	31	Hentriacontane
14	Tetradecane	32	Dotriacontane
15	Pentadecane	33	Tritriacontane
16	Hexadecane	40	Tetracontane
17	Heptadecane	50	Pentacontane
18	Octadecane	60	Hexacontane

The name of the straight-chain alkane of eleven carbon atoms has long been in dispute. Some prefer *undecane* and some *hendecane*. The Fifteenth Conference of I.U.P.A.C. selected undecane for eleven carbon atoms, but heneicosane and hentriacontane for twenty-one and thirty-one. The reasoning is obscure. At least one paper has sought to solve the problem by calling the compound hendecane, but the radical undecyl.

Incidentally, there is no basis save frequent usage for "n-heptane," "n-octane," and so on. Other alkanes of seven carbon atoms are not heptanes, but substituted hexanes, pentanes or butane.

*Alkenes* are named by substituting, for the *ane* endings of the corresponding alkanes, the endings *ene*, *diene*, *triene*, etc., and indicating the position of the double bond or bonds, using the lowest possible numbers.

*Alkynes* are similarly named by substituting the endings *yne*, *diyne*, etc.

Aliphatic compounds containing both double and triple bonds have the ending *enyne*. In numbering the double and triple bonds, lower numbers are assigned to the double bonds.

Examples:      •••••• Hexane  
                   •••••• 2-Hexene (not 4-Hexene)  
                   •••••• 2,4-Hexadiene  
                   •••••• 3-Hexyne  
                   •••••• 1-Hexen-4-yne (not 5-Hexen-2-yne)

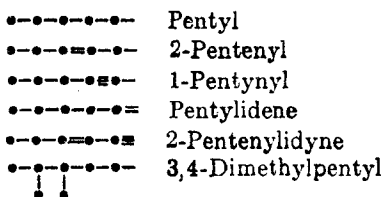
The above representations of aliphatic structures are not the customary

ones, but have been found much more convenient than those which "spell out" all the C and H atoms. After all, there is no more need to show each C and H in a chain than in a benzene or cyclohexane ring. It seems to the writer that the salient features of various chains stand out more clearly in the above type of skeleton than when letters are employed.

A *univalent radical* derived from a straight-chain *alkane* by removal of a hydrogen from a terminal carbon atom is named by substituting, in the name of the alkane, the ending *yl* for the ending *ane*. The carbon atom having the free valency is numbered as 1.

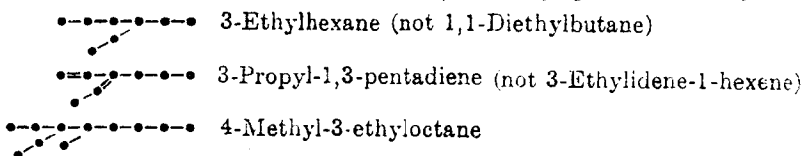
A *univalent radical* from an *alkene* or *alkyne* is named by dropping the final *e* from the hydrocarbon name and adding *yl*.

*Bivalent radicals* (double bond at the point of attachment) are named by adding the ending *idene* to the name of the corresponding univalent radical. *Trivalent radicals* are named similarly, except that the ending is *idyne*.

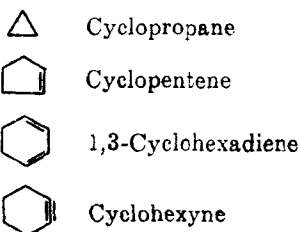


*Branched-chain hydrocarbons* are named as derivatives of the longest chain present in the formula, assigning the lowest possible numbers to the side chains. If, however, unsaturation is present in the molecule, that chain is chosen as the parent which contains the maximum number of double and triple bonds, whether or not it is the longest chain.

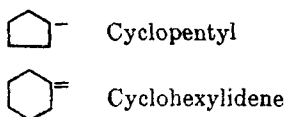
With respect to the order in which substituents should be named, Rule 7 of the Definitive Report first states that the order will be that of their "complexity," without stating whether the least or most complex should be first, and then adds that the alphabetic order may also be followed. *Chemical Abstracts* employs the latter, and there doubtless are advantages for indexing purposes, but the writer prefers a specific modification of the former. Substituents are given in order of increasing weight; when substituents are of the same weight the least complex is named first, e.g., butyl, isobutyl. The single exception is hydrogen. In the case of 1,2,3,4-tetrahydronaphthalene, it is considered that the addition of hydrogen merely changes the parent compound, and substituents such as methyl or ethyl precede the "hydro."




*Cyclanes*, *cyclenes* and *cyclynes* are named by prefixing *cyclo* to the names of the acyclic hydrocarbons having corresponding numbers of carbon atoms:



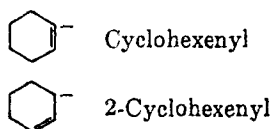
Naming of radicals is similar to the naming of acyclic radicals:



There is, however, one slight difference in the handling of unsaturated cyclics as compared to unsaturated acyclics. With unsaturated chains it is always necessary to specify the positions of the double or triple bonds, but with cyclenes such numbering may frequently be omitted.

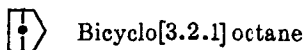
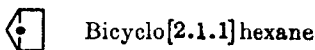
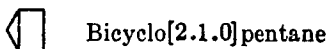
 is 3,4-Dimethylcyclohexene, because numbering starts with the double bond.

With radicals, the position of the double bond must be stated if it does not coincide with the point of attachment, with which numbering starts unless, as stated by the I.U.P.A.C., "the enumeration has previously been established."



*Bicyclic* and *tricyclic* non-aromatic compounds are usually named, in the Handbook, by the Baeyer system. For a bicyclic compound the formula is drawn so that the bridge contains as few carbon atoms as possible, with the larger ring at the right and the smaller ring at the left. Bracketed figures indicate, in that order, the number of carbon atoms in the right ring, the left ring, and the bridge respectively. After the bracket is given the name of the hydrocarbon indicating the total number of carbon atoms, which is always two greater than the sum of the figures (other than superscripts) enclosed

in the bracket.



Numbering starts at one end of the bridge, proceeds around the larger ring and back to the starting point, and then along the bridge, if carbon atoms occur in the bridge.



For *tricyclic compounds* the position of the second bridge is indicated by superscripts.



Tricyclo[2.2.1.0<sup>2,6</sup>]heptane

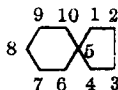
The presence of double bonds can readily be shown.



Bicyclo[2.2.1]-2-heptene

If aromatic rings are present, however, the Baeyer system should not be used, since the numbering would indicate the double bonds to be fixed.

*Spiro compounds* are those in which a single atom is the only one common to two rings. For spiro hydrocarbons it is customary (contrary to the practice for bicyclic compounds) to write the formula with the smaller ring at the right, and to begin numbering with the first free carbon in the right ring. The number of atoms in each ring, not counting the common atom, is indicated by bracketed numbers.

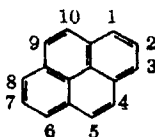


Spiro[4.5]decane

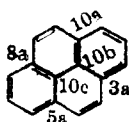
Relatively few of the names of the basic *aromatic hydrocarbons* are systematic; naphthalene, anthracene, phenanthrene, fluorene, indene, acenaphthylene and so on may all, like benzene, be termed trivial names.

In numbering polycyclic aromatic structures, the formula is written with the greatest possible number of rings in a horizontal row, and with the maximum number of rings above and to the right. Numbering begins with

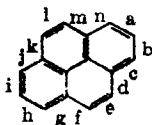
the first free angle (an angle which is a part of but one ring) of the upper right ring, and proceeds clockwise, omitting those atoms common to two or more rings.



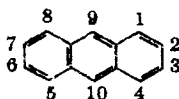
The atoms common to two or more rings but on the "outside" of the formula are numbered by adding a, b, etc. to the numbers of the immediately preceding "free" atoms. Interior atoms are numbered by adding letters to the highest number.



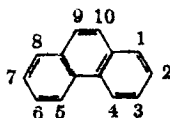
Sides may be indicated by letters. The side between 1 and 2 becomes a, and others are lettered alphabetically and clockwise.



Anthracene, phenanthrene, and the cyclopenta[a]phenanthrenes are, in deference to usage, exceptions to the above rules for numbering. For anthracene, numbering starts normally, but then jumps from the first to the third ring and back to the second.

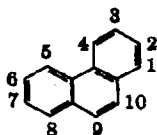


In the case of phenanthrene there are two methods. *Chemical Abstracts* first orients the formula incorrectly, and the numbering is clockwise.



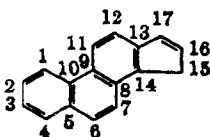
Mary Alexander, in her paper presented before the Joint Symposium on Nomenclature of Hydrocarbons, orients the formula correctly, after which

numbering becomes counter-clockwise.



Although it is a Hobson's choice, the latter is chosen.

Cyclopenta[a]phenanthrene does a very thorough job of violating the rules.



Cyclopenta[a]phenanthrene is an example of a cyclic structure in which there occurs a hydrogen which is necessary to the existence of the least hydrogenated form, but which may be in any of two or more positions. This is indicated by prefixing the numerical position to H, so that the full name of the form just shown is 15H-cyclopenta[a]phenanthrene. If the double bond were between positions 15 and 16, the name would be 17H-cyclopenta[a]phenanthrene.

In the naming of highly hydrogenated forms of two-ring aromatic hydrocarbons such as naphthalene, indene, and heptalene, the Handbook departs from the method of *Chemical Abstracts Index*, and employs the Baeyer system, as did Egloff. It is well accepted that the names cyclohexene and cyclohexane are preferable to dihydrobenzene and hexahydrobenzene, because the compounds are not aromatic in character. Similarly, decahydronaphthalene is not aromatic, and it would therefore seem better to call it bicyclo[4.4.0]decane.

In many cases the Baeyer scheme provides much simpler names.



1,2,3,4,4a,5,8,8a-Octahydronaphthalene  
Bicyclo[4.4.0]-3-decene



1,2,3,4,5,5a,6,7,10,10a-Decahydroheptalene  
Bicyclo[5.5.0]-3-dodecene

There is, however, no alternative to 1,2,3,4-tetrahydronaphthalene, first because, as pointed out above, the Baeyer system is not applicable, and second because the compound is still aromatic and that fact should be indicated by the name.

Use of the Baeyer system does have one unfortunate consequence, in that the numbering of substituents is changed in going from an aromatic to a bicyclic parent, because numbering of the aromatic starts with the free angle, whereas numbering of the bicyclic starts with the end of the bridge.

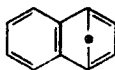


1-Methyldecahydronaphthalene

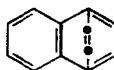
2-Methylbicyclo[4.4.0]decane

The highly hydrogenated forms of three-ring aromatic hydrocarbons may be named as tricyclic compounds. Tetradecahydroanthracene is tricyclo[8.4.0.0<sup>3,8</sup>]tetradecane, while tetradecahydrophenanthrene is tricyclo[8.4.0.0<sup>2,7</sup>]tetradecane. Such usage, however, is rare, and was not adopted for the Handbook.

For bridged compounds which cannot conveniently be named by the Baeyer system, the carbon atoms in each bridge may be named as a multi-valent radical:



1,4-Methanonaphthalene



1,4-Ethenonaphthalene

The names of complex least hydrogenated cyclic compounds are "built up" as follows.

One of the long-established compounds, usually an aromatic, is selected as the parent. Most of the names of such compounds are non-systematic, and therefore relatively short. That parent is chosen which is as large as possible, preferably linear, and permits attached components of the smallest size, with the least number of sides common to parent and attached components.

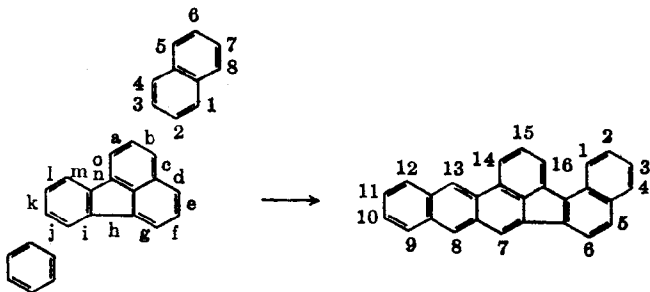
In expressing the new name, the numbering or lettering of parent and components is employed, but the new formula is always renumbered. If necessary, the new formula is reoriented before renumbering.

*Benz[a]anthracene* needs no reorientation, but does require renumbering:

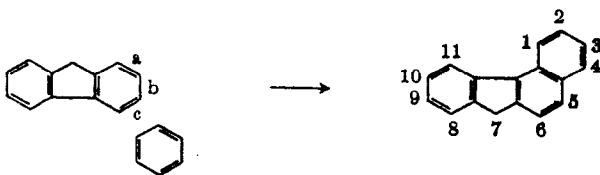


It will be noted that the unconventional numbering of anthracene is eliminated in the renumbering.

*Benzo[j]naphtho[2,3-b]fluoranthene* requires reorientation before renumbering:



*7H-Benzo[c]fluorene* must be reoriented before renumbering, and the position of the extra hydrogen must be given:



Two important principles of *Chemical Abstracts* are followed, with but few exceptions. The first is that of selecting the *largest parent*, whereby

is called ethylbenzene and not phenylethane. The second is *like treatment of like things*, being known as diphenylmethane and not benzylbenzene.

Exceptions to the largest parent principle are in the interest of simplicity of name. For example, 1-tridecyl-naphthalene appears preferable to 1-(1-naphthyl)tridecane.

The question of the use of non-systematic names for radicals or parent compounds is knotty. Dr. Crane has succinctly expressed one side of the argument: "They are useful in naming derivatives, for purely systematic names often become unmanageably long and complicated." Well, almost unmanageably, but on the other side lies the difficulty of associating the proper structures with a few dozen names such as benzohydryl, camphanyl, carvacryl, crotyl, duryl, fenchyl, hydnocarpyl, menthyl, norcamphyl, and thujyl. The writer prefers the systematic names, but has used most of the non-systematic ones upon which both *Chemical Abstracts* and I.U.P.A.C.



agree, plus a few recommended by the latter. They are given in the following table.

*Non-Systematic Radicals Used by the Handbook*

Allyl $\cdot = \text{CH}_2 - \text{CH} \cdot$	Isohexyl $\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CH}_3$ but note that
Benzyl $\text{C}_6\text{H}_5 - \cdot$	$\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ is 5-Methylhexyl
Biphenylyl : from $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5$	Isopropenyl $\cdot = \text{C}(\text{CH}_3) - \text{CH}_2 \cdot$
sec-Butyl $\cdot - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_3$	Mesityl $\cdot - \text{C}_6\text{H}_2(\text{CH}_3)_3$
tert-Butyl $\cdot - \text{C}(\text{CH}_3)_3$	Methylene $\cdot = \text{CH}_2$
Cinnamyl $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \cdot$	Neopentyl $\cdot - \text{C}(\text{CH}_3)_3$
Isopropyl $\cdot - \text{CH}(\text{CH}_3)_2$	Phenethyl $\text{C}_6\text{H}_5 - \text{CH}_2 - \cdot$
Isobutyl $\cdot - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$	Styryl $\text{C}_6\text{H}_5 - \text{CH} = \cdot$
Isopentyl $\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{CH}_3$	Tolyl (o,m,p) : from $\text{C}_6\text{H}_4(\text{CH}_3) - \cdot$

The following table is given for reference purposes.

*Non-Systematic Radicals Used by Chemical Abstracts  
but not by the Handbook*

Amyl $\cdot - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$	Benzohydryl $\text{C}_6\text{H}_5 - \text{C}(\text{C}_6\text{H}_5)_2 - \cdot$
tert-Amyl $\cdot - \text{C}(\text{CH}_3)_3 - \text{CH}_2 - \text{CH}_3$	Camphanyl : from $\text{C}_{10}\text{H}_{17} - \cdot$