

THE CHEMICAL SOCIETY

# Annual Reports

On The Progress  
Of Chemistry

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FOR 1970

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Volume 67  
Section B

THE CHEMICAL SOCIETY

# Annual Reports

On The Progress  
Of Chemistry

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Volume 67  
Section B

ORGANIC CHEMISTRY

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*Section A, General, Physical, and Inorganic Chemistry, contains  
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- 2 Determination and Interpretation of Molecular Wave  
Functions. By E. Steiner
- 3 Theories of Dense Fluids. By I. R. McDonald and K. Singer
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Complexes. By P. S. Braterman
- 16 Mechanisms of Inorganic Reactions. By A. McAuley

## PREFACE

IT IS THE continuing policy of *Annual Reports on the Progress of Chemistry*, as described in the Preface to the 1967 Reports (Volume 64), that these volumes should attempt to provide critical coverage of significant work in any given field, rather than a comprehensive cataloguing of references. It is hoped that this shift in emphasis will accelerate in succeeding volumes, as the *Specialist Periodical Reports* series, designed to describe progress in specialised areas of chemistry in detail, grows to its full complement of titles (35-40 planned to be in production by 1973) which will provide comprehensive coverage of the whole field of Chemistry.

By the end of 1971 the *Specialist Periodical Reports* series will consist of 15 titles, with 26 available volumes. The first volumes of 8 new titles will be published in 1972 with a further 4-6 titles in 1973.

Since the publication of the 1969 Annual Reports the following new titles have been produced: **Organic Compounds of Sulphur, Selenium, and Tellurium** (Senior Reporter, Dr. D. H. Reid, University of St. Andrews); **Electrochemistry** (Senior Reporter, Professor G. J. Hills, University of Southampton); **Mass Spectrometry** (Senior Reporter, Dr. D. H. Williams, Cambridge University); **Foreign Compound Metabolism in Mammals** (Senior Reporter, Dr. D. E. Hathway, Huntingdon Research Centre); **The Alkaloids** (Senior Reporter, Dr. J. E. Saxton, University of Leeds); **Inorganic Reaction Mechanisms** (Senior Reporter, Dr. J. Burgess, Leicester University); and **Terpenoids and Steroids** (Senior Reporter, Dr. K. H. Overton, Glasgow University).

Titles which will be in production before the publication of the 1972 Annual Reports include: **Fluorocarbon and Related Chemistry** (Senior Reporters, Dr. R. E. Banks and Dr. M. G. Barlow, University of Manchester Institute of Science and Technology); **Electronic Structure and Magnetic Properties of Inorganic Compounds** (Senior Reporter, Dr. P. Day, Oxford University); **Chemical Thermodynamics** (Senior Reporter, Professor M. L. McGlashan, University of Exeter); **Radiochemistry** (Senior Reporter, Dr. G. W. A. Newton, Manchester University); **Surface and Defect Properties of Solids** (Senior Reporters, Professor M. W. Roberts, University of Bradford, and Professor J. M. Thomas, University College of Wales); **Nuclear Magnetic Resonance** (Senior Reporter, Dr. R. K. Harris, University of East Anglia); **Inorganic Chemistry of the Transition Elements** (Senior Reporter, Dr. B. F. G. Johnson, Cambridge University); **Organometallic Chemistry** (Senior Reporters, Professor F. G. A. Stone and Dr. E. W. Abel, University of Bristol); **Molecular Structure** (Senior Reporters, Professor G. A. Sim, Glasgow University, and Dr. L. E. Sutton, University of Oxford); **Colloid Science** (Senior Reporter,

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# ORGANIC CHEMISTRY

## 1 Introduction

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By G. W. KIRBY

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and R. O. C. NORMAN

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THE areas of Organic Chemistry which are surveyed this year continue last year's pattern with the following exceptions. Sections on Nucleic Acids and Enzyme Mechanisms, effectively covering two years, have been reintroduced, while that on Amino-acids and Peptides has been temporarily omitted. Attention is drawn to the availability of Specialist Periodical Reports on the last topic and also on Photochemistry; the initiation of the latter series has led us to include only a very brief Report on this topic. The following are some of the more notable features reported on in 1970 and surveyed in greater detail in this Volume.

The crystallographic work during the year is notable for its observable trends rather than particular reports. Thus, direct methods are being increasingly used, especially in the case of non-centrosymmetric structures, and this independence from the heavy atom has resulted in an improvement in quality and accuracy in the determination of such structures. In the application of X-ray crystallography, the most notable features are the investigations of biologically active molecules, where the crystallographic information can yield direct evidence of structure-activity relationships in the biological systems.

Mechanistic studies have been mainly concerned with the consolidation of recent developments. For example, further instances have been reported of the inadequacy of Brönsted slopes, when compared with isotope effects, as a measure of the position of the transition state along the reaction path; there has been further speculation on the role of pseudorotation in nucleophilic displacement at phosphorus in cyclic esters and related compounds; and there is now a more complete understanding of the role of the solvent in ionisation processes—of particular significance in this respect is Schleyer's use of the 2-adamantyl system as a model by which to measure the importance of the ionisation pathway and thus to separate it from the solvent-displacement pathway. Carbonium-ion chemistry remains active, and there is now strong evidence for the occurrence of vinyl cations, especially from 1-arylethyl halides and sulphonates in highly ionising media. Formidable evidence in favour of the non-classical representation of the 7-norbornenyl cation is the culmination of work in this area by Winstein.



The isolation of stable dialkylhalonium salts,  $R_2\text{Hal}^+ \text{SbF}_6^-$ , is noteworthy, and their ability to cleave ethers readily may be of practical use.

As anticipated, the photolytic decomposition of peroxides and azo-compounds has been increasingly employed to obtain e.s.r. spectra from structurally interesting radicals; analysis of the results together with calculations based on the widely used INDO method have enabled detailed conclusions about hybridisation and delocalisation to be drawn. One interesting innovation has been the radiolytic generation of trapped radicals exhibiting isotropic spectra within a host lattice of, for example, adamantane. An extension of the theory of chemically induced dynamic nuclear polarisation (CIDNP), which allows the form of the spectrum of a product with several nuclear spins to be predicted, significantly enhances the value of this increasingly popular tool. In addition, further examples of emission and enhanced absorption phenomena for radicals in solution have been characterised, and the recognition of a relationship between these effects and CIDNP indicates that interesting developments in the relevant relaxation theory can be expected. As to the reactions of radicals, further insight has been gained into the nature and rates of processes which are undergone by geminate pairs of free radicals (from peroxides or azo-compounds) before they can escape from the solvent cage.

The process of intermolecular energy transfer continues to attract much attention and it now seems that a Schenck mechanism may be involved in a number of cases of *cis-trans* isomerization of olefins. Interpretation of results with triphenylene as a triplet sensitizer and penta-1,3-diene for detection of triplet states must, it appears, be made with caution, as respective sensitisation and quenching of singlet states can also occur. 'Dewar pyridine' has been isolated from the photolysis of pyridine and has been shown to be the intermediate in the light-induced hydration of pyridine to form 5-aminopenta-2,4-dienal. The importance of charge-transfer phenomena in photochemistry has been reported this year from such diverse areas as vinyl polymerisation initiation, fluorescence quenching, and acid-catalysis investigations.

The versatility of transition-metal complexes in organic synthesis is now well recognised. Hydrogenation, carbon monoxide insertion, and carbon-carbon bond formation (as in dimerisation) are already well established, but relatively new reactions such as carbon skeletal isomerisation and olefin disproportionation could play an increasing role in preparative chemistry. The introduction of heteroatoms into organic compounds is illustrated by nucleophilic attack and reaction with sulphur compounds; the removal of heteroatoms can be effected by decarbonylation and the reaction of low-valent metal carbonyls to remove oxygen from molecules.

Interest continues to be shown in the synthesis of complex natural products and of molecules containing reactive structural features. The development of new reagents is often a necessary adjunct to extended synthetic projects, while the modification of established methods may also be important. For example, useful variants on the familiar hydridic reductions have appeared. Thus lithium cyanohydridoborate reduces ketones more slowly than do the common borohydrides

but is stable at low pH; under these conditions exchange of hydrogen with the aqueous medium is rapid, permitting reductive deuteration and tritiation. The reagent attacks imines more rapidly than ketones at  $\text{pH} < 7$  and can therefore be used for the reductive amination of carbonyl compounds. Also, the discovery that the borohydride anion can under defined conditions exchange hydrogen with protic solvents has led to a simple method for reductive tritiation. Use of the trimethylsilyl protecting group has been extended into acetylene chemistry. Terminal acetylenes can be silylated in the usual way: the products still show the characteristic reactions of the acetylenic triple bond and removal of the protecting group is readily effected. The conversion of olefins into iodohydrins can now be readily accomplished and the products may serve as efficient precursors for oxirans. The preparation of tetrasubstituted olefins by linkage of the appropriate disubstituted moieties is often difficult, but the use of double extrusion reactions involving loss of, for example, sulphur, nitrogen, or carbon dioxide from a cyclic intermediate affords in certain cases an efficient solution to this problem. The Cope rearrangement of 1,2-divinyl alcohols and glycols has provided a useful and stereospecific route to medium-ring ketones. A double Cope rearrangement of a vinyl allyl ether has been used in a synthesis of the furanoaldehyde, torreyal. The synthesis of methyl natural bixin confirms the structure previously assigned to this compound and provides the first stereochemically controlled synthesis of a carotenoid having a trisubstituted *cis*-double bond. Loganin, a key intermediate in the biosynthesis of the indole alkaloids, has been synthesised, with predictable elegance, by Büchi's group; the successful route to this highly oxygenated and reactive molecule involved a variant of de Mayo's reaction, namely the photochemical addition of a cyclopentene to an enolised  $\beta$ -tricarbonyl derivative. In van Tamelen's synthesis of the indole alkaloid, ajmaline, generation of an important iminium ion intermediate was achieved by decarbonylation of an  $\alpha$ -amino-acid using dicyclohexylcarbodi-imide and toluene-*p*-sulphonic acid. A resurgence of interest in the chemistry and pharmaceutical use of quinine has led to a new stereoselective total synthesis and a partial synthesis of this and related alkaloids.

The reintroduction this year of an article on Nucleic Acids is in time to report two outstanding achievements. Khorana's preparation of a gene, consisting of a helical duplex of 77 base-pairs, marks the completion of the largest controlled synthesis yet attempted while Beckwith's isolation of the DNA of a single operon is perhaps the most ingenious purification of a natural product yet recorded.

The bridged annulenes, a group of interesting, non-benzenoid aromatic compounds, have been studied intensively by Vogel's group at Köln during the last few years. A review of their chemistry has now appeared and new examples of the class reported. A ten-electron analogue of tropone has the spectroscopic and chemical properties expected of a polyenone but the protonated form is, as expected, aromatic. Several double-bridged [14]annulenes have been obtained: the syntheses were, necessarily, long but sufficient material was obtained for full spectroscopic characterisation. Elegant new syntheses of bridged annulenes of a different kind, those based on the dihydropyrene system, have been developed.

by Boekelheide's group. The preparation of strained and reactive molecules continues to provide sport for the experimentalist and entertainment for the reader. The 'Dewar analogue' of *o*-xylene can be isolated at low temperature although the parent 'benzenoid' compound has only a transient existence. Dioxetans have been prepared by the photochemical oxygenation of electron-rich olefins. The reaction is stereospecific and may involve antarafacial addition of singlet oxygen to the olefin; thus *cis*- and *trans*-diethoxyethylene gave, respectively, *cis*- and *trans*-diethoxy-1,2-dioxetan. 1,2-Naphthalene oxide has been obtained in partially resolved form and found to be optically stable at ambient temperatures, confirming an earlier conclusion that this arene oxide is not in equilibrium with the corresponding oxepin. The first isolable compound, a thiacycloheptyne, containing an acetylenic linkage in a 7-membered ring has been reported.

A most interesting development in alicyclic chemistry has arisen with the observation that silver, and other transition-metal, salts can catalyse the rearrangement of strained, saturated ring systems. Purification of a bis-homocubane derivative on a silica-silver nitrate column was found to have induced, fortuitously, isomerisation to another pentacyclic derivative now containing two cyclopropane rings. Independent observations of the isomerisation of several other saturated polycycles soon appeared. Cubane itself is converted by silver(I) or palladium(II) into the new pentacyclo-octane, 'cuneane'. These discoveries have already led to an efficient, rational synthesis of semi-bullvalene. In general, the isomerisations proceed at room temperature whereas the corresponding uncatalysed, thermal processes are orbital-symmetry disallowed and either do not occur or take place only at high temperatures. It is still not clear whether discrete organometallic intermediates are involved in the overall transformations.

A glance through the sections on Alicyclic, Aromatic, and Heterocyclic chemistry will reveal the considerable current interest in thermal rearrangements and thermolyses. Some of this work has doubtless been stimulated by the search for exceptions ('there are none') to the Woodward-Hoffmann Rules; certainly the Rules provide an essential guide through the maze of consecutive transformations shown by so many cyclic, unsaturated compounds. The rearrangement of bromocyclo-octatetraene to  $\beta$ -bromostyrene has been shown to involve valence-tautomerism, ionisation and ion recombination, and a final electrocyclic ring opening, the whole process being highly stereoselective. The *para* or Claisen rearrangement of hexa-2,4-dienyl phenyl ether provides the first clear example of a [5s,5s]sigmatropic rearrangement proceeding through a 10-membered transition state.

Biosynthetic studies this year have been characterised more by the detailed examination or critical re-examination of familiar processes than by the discovery of new pathways. Lynen has purified an enzyme responsible for the production of the simple polyketide, 6-methylsalicylic acid, in *P. patulum*; the enzyme uses acetyl-CoA and malonyl-CoA as substrates and requires NADPH for the necessary removal of one oxygen function. Apparently, only one enzyme is involved and no intermediates have been detected. Büchi's scheme for the

biosynthesis of the aflatoxins has received experimental support and the biosynthesis of gliotoxin from phenylalanine is now considered to involve an arene oxide rather than *m*-tyrosine as an intermediate.

Progress has continued to be made towards the understanding of the course of enzyme-catalyzed reactions in terms of the language of mechanistic organic chemistry. Studies on the coenzyme-B<sub>12</sub> linked enzymic reactions have revealed the participation of the C-5' of the coenzyme during catalysis. Modified amino-acid residues present in polypeptide chains of enzymes have been shown to be prosthetic groups in several biological transformations.



## 2 Physical Methods

### Part (i), Mass Spectroscopy

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By R. T. APLIN

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DURING 1970 the number of papers on this topic has further increased,\* notably in areas of applied mass spectrometry, particularly in the natural product and biochemical fields. There has also been an increase in the number of papers concerned with detailed studies of the kinetics and mechanisms of fragmentation processes. Two new techniques, ion cyclotron resonance<sup>1</sup> (ICR) and ion kinetic energy spectroscopy<sup>2</sup> (IKES), have been employed in the interpretation of various fragmentation processes. This Report will attempt to cover the more generally interesting aspects of both the detailed and applied papers.

**General Methods of Interpretation.**—The quasi-equilibrium theory (QET), whose validity for small molecules is well established, has been shown to give rate constants which agree well with those observed from a study of substituent effects on normal and metastable ion abundances, as well as ionisation and appearance potentials of 1,2-diphenylethanes.<sup>3</sup> A probability distribution of internal energies has been derived<sup>4</sup> for those aromatic molecular ions which undergo decomposition to afford a single product whose relative abundance and appearance potential are each functions of Hammett sigma constants. This approach provides a rationalisation for the unexpected relationship between sigma constants and the loss of substituents from biphenyl molecular ions.<sup>5</sup> Both +I and -I substituents are capable of increasing the migratory aptitude of aryl groups in the spectra of diaryl sulphones. This rearrangement also affords a Hammett correlation with total ion abundances at 20 eV.<sup>6</sup>

**Ion Energies and Structure.** The production and subsequent decomposition of benzoyl ions ( $m/e$  105) derived from *N*-(substituted phenyl)benzamide (1) are related to the energy distribution in the molecular ion.<sup>7</sup> The substituent effects

<sup>1</sup> G. C. Goode, R. M. O'Malley, A. J. Ferrer-Correia, and K. Jennings, *Chem. in Britain*, 1971, 7, 12.

<sup>2</sup> J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, 3, 313.

<sup>3</sup> F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *J. Amer. Chem. Soc.*, 1970, 92, 6867.

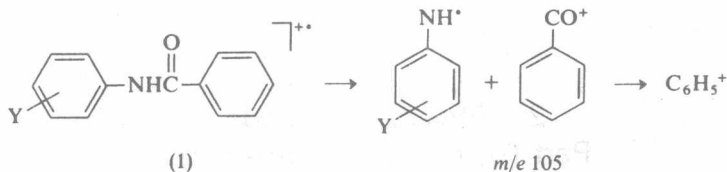
<sup>4</sup> R. P. Buck and M. M. Bursey, *Org. Mass Spectrometry*, 1970, 3, 387.

<sup>5</sup> M. M. Bursey and P. T. Kissinger, *Org. Mass Spectrometry*, 1970, 3, 395.

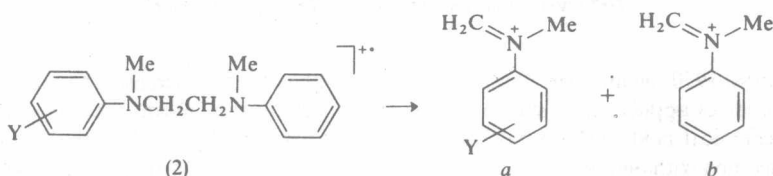
<sup>6</sup> T. Nagai, T. Maeno, and N. Tokura, *Bull. Chem. Soc. Japan*, 1970, 43, 462.

<sup>7</sup> R. H. Shapiro, J. Turk, and J. W. Serum, *Org. Mass Spectrometry*, 1970, 3, 171.

\* Many of the papers are mentioned in the first volume of 'Mass Spectroscopy', ed. D. H. Williams (Specialist Periodical Report), The Chemical Society, London, 1971.

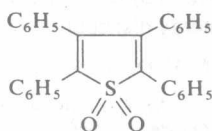
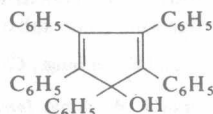
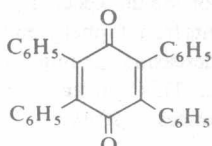
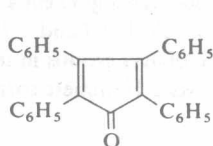


observed in the spectra of *NN'*-diarylethylenediamines (2) are best interpreted as affording the fragments (a) and (b) with open-chain rather than the closed structures



shown.<sup>8</sup> Electron-withdrawing substituents increase the abundance of the molecular ion in the spectra of substituted styrene ozonides; the intensities of the fragments  $X \cdot C_6H_4 \cdot CHO^{+ \bullet}$  follow a Hammett relationship.<sup>9</sup> Ground-state bond-orders in molecular ions derived from MO analysis can be used as a reliable guide to the low-energy (ground-state) fragmentation of heterocycles.<sup>10</sup>

The subsequent decomposition of the  $M - 42$  ions derived from methoxy- and dimethoxy-phenyl acetates<sup>11</sup> suggests that these ions have the structure of the corresponding phenols. <sup>13</sup>C Labelling has established that the  $[C_6H_6O]^{+ \bullet}$  ion in the spectrum of  $C_6H_5OC_4H_9$  has the same structure as the phenol molecular ion.<sup>12</sup> Steric effects suggest that the  $[YC_6H_5N]^{+ \bullet}$  ions from phenyl-substituted acetanilides have the structure of the corresponding aniline.<sup>13</sup> A study of appearance potentials and metastable ion abundances has shown that the  $m/e$  165 ions



<sup>8</sup> H. Giezendanner, M. Hesse, and H. Schmid, *Org. Mass Spectrometry*, 1970, 4, 405.

<sup>9</sup> J. Carles, Y. Rousseau, and S. Fliszar, *Canad. J. Chem.*, 1970, 48, 2345.

<sup>10</sup> R. C. Dougherty, R. L. Foltz, and L. B. Kier, *Tetrahedron*, 1970, 26, 1989.

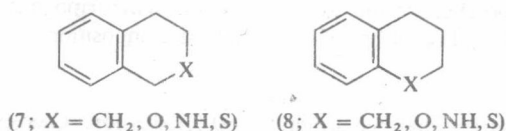
<sup>11</sup> C. B. Thomas, *J. Chem. Soc. (B)*, 1970, 430.

<sup>12</sup> P. D. Woodgate and C. Djerassi, *Org. Mass Spectrometry*, 1970, 3, 1093.

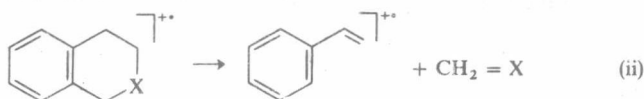
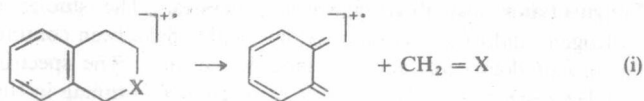
<sup>13</sup> A. A. Gamble, J. R. Gilbert, and J. G. Tillet, *Org. Mass Spectrometry*, 1970, 3, 1223.

( $C_{13}H_9^+$ ) from fluorene and phenalene do not have the same structures;<sup>14</sup> similarly, the ions  $C_{13}H_9^+$  and  $C_{12}H_9N^+$  from 1-(benzylideneamino)benzotriazole do not have the fluorenyl or carbazole structures.<sup>15</sup> *p*-Fluoro-labelling has established that the  $(C_2Ar_2)^{++}$  ions derived from tetracyclone (3) and tetraphenylquinone (4) are produced after complete scrambling in the molecular ion, that partial scrambling occurs in pentaphenylcyclopentadienol (5), and that there is virtually no scrambling in tetraphenylthiophen SS-dioxide (6).<sup>16</sup>

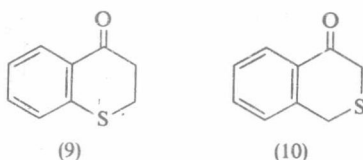
A detailed study of the fragmentation of tetralin and related heterocycles [(7) and (8)] has shown that only isothiochroman (7; X = S) gives a true retro-Diels-Alder (RDA) fragmentation. In the series (7; X = O, NH, and S) the ion of



*m/e* 104 is produced almost exclusively by process (i). However, for tetralin only 45% is produced by this route, the remainder by (ii). In the series of compounds



(8) the RDA fragmentation is not important.<sup>17</sup> The spectra of the related systems (9) and (10) are dominated by processes equivalent to (i).<sup>18</sup>



The full details of the ICR study of the double McLafferty rearrangement reported last year<sup>19</sup> have appeared.<sup>20</sup> The subsequent decomposition of the enol

<sup>14</sup> J. H. Bowie and T. K. Bradshaw, *Austral. J. Chem.*, 1970, **23**, 1431.

<sup>15</sup> U. Rapp, H. A. Staals, and C. Wunsche, *Org. Mass Spectrometry*, 1970, **3**, 45.

<sup>16</sup> M. K. Hoffman, T. A. Elwood, P. F. Rogerson, J. M. Tesaret, M. M. Bursay, and D. Rosenthal, *Org. Mass Spectrometry*, 1970, **3**, 891.

<sup>17</sup> A. G. Loudon, A. Maccoll, and S. K. Wong, *J. Chem. Soc. (B)*, 1970, 1727.

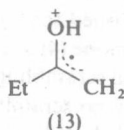
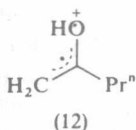
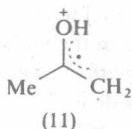
<sup>18</sup> A. G. Harrison, M. T. Thomas, and I. W. J. Still, *Org. Mass Spectrometry*, 1970, **3**, 899.

<sup>19</sup> G. Eaden, J. Dickmann, and C. Djerassi, *J. Amer. Chem. Soc.*, 1969, **91**, 3986.

<sup>20</sup> G. Eaden, J. Dickmann, and C. Djerassi, *J. Amer. Chem. Soc.*, 1970, **92**, 6205.



ions (11), (12), and (13) produced in the McLafferty rearrangement of simple ketones is *via* initial ketonisation.<sup>21</sup>

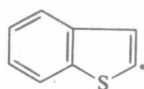
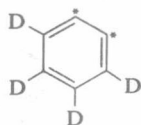
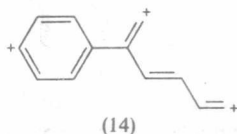


The technique of ion kinetic energy spectroscopy (IKES) has been applied to study the processes involved and the energetics of the spectra of a series of aromatic hydrocarbons,<sup>22</sup> and also used to study the triply charged molecular ion of biphenyl.<sup>23</sup> The release of 4.5 eV in its decomposition:



suggests the charge-separated structure (14) for this ion. Conventional spectra have also been used to study similar processes in other condensed aromatic compounds.<sup>24</sup>

**Fragmentation and Rearrangement Processes.**—The studies of carbon and hydrogen randomisation reported last year<sup>25</sup> have been continued this year by the use of deuterium and <sup>13</sup>C-labelled systems. The spectrum of the <sup>13</sup>C-labelled benzene (15) shows complete carbon scrambling in the molecular ion prior to the loss of C<sub>2</sub>H<sub>2</sub>.<sup>26</sup> The spectrum of the doubly labelled benzene (16)



(15) \* = <sup>13</sup>C

(16)

(17)

showed that *ca.* 30% of the ions C<sub>3</sub>H<sub>3</sub><sup>+</sup> and C<sub>4</sub>H<sub>4</sub><sup>+</sup> arise by paths in which the carbon atoms are scrambled *without* breaking C—H bonds. In the remaining 70% the hydrogens are scrambled over and beyond whatever carbon scrambling

<sup>21</sup> D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 6343.

<sup>22</sup> J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrometry*, 1970, **3**, 455.

<sup>23</sup> J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrometry*, 1970, **3**, 661.

<sup>24</sup> P. Nounou, *Internat. J. Mass Spectrometry Ion Phys.*, 1970, **4**, 219.

<sup>25</sup> R. T. Aplin, *Ann. Reports (B)*, 1969, **66**, 5.

<sup>26</sup> I. Hormon, A. N. Yeo, and D. H. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 2131.