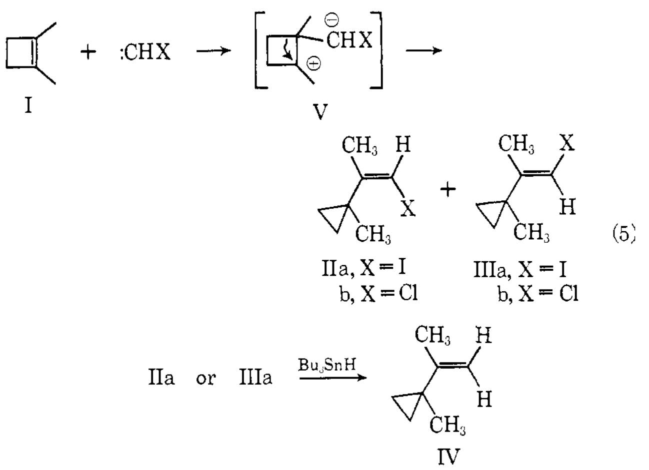
may proceed *via* a dipolar intermediate (V) which subsequently rearranges to give vinylcyclopropanes II and III as the final products (reaction 5).



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[9] National Institutes of Health Predoctoral Fellow, 1967–1968.

[10] The authors thank Professors G. L. Closs and L. Kaplan for many stimulating and helpful discussions.

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Photolysis of Benzene Vapor at 1849 Å. Formation of *cis*-1,3-Hexadien-5-yne[1]

Sir:

In two recent studies[2,3] of the photolysis of benzene vapor at 1849 Å, benzene was found to disappear with high quantum yield forming two major products: polymer and an isomer with a highly structured absorption spectrum centered near 2350 Å. This isomer was subsequently identified[4,5] as fulvene. We now wish to report that an open-chain isomer, *cis*-1,3-hexadien-5-yne, is also formed from benzene vapor at 1849 Å. Studies of the photochemistry of the products in the vapor phase reveal that they undergo isomerization both at 1849 and 2537 Å.

Most of the irradiations in the present study were performed in an atmosphere of N_2 in a silica cell 2 cm in diameter and 10 cm long. A 1-cm cell of the same diameter was used for benzene at pressures above 1 torr. The cells were filled by flushing either with N_2 saturated with benzene at an appropriate temperature or with a chromatographic effluent containing fulvene or hexadienyne. They were irradiated with a flat helical Suprasil Hg-resonance lamp, using either a γ-irradiated LiF filter[6] to exclude 2537-Å radiation or a Corning 7910 filter to exclude 1849-Å radiation. The input to the cell was 4×10^{15} quanta/sec of 1849-Å radiation or 2×10^{16} quanta/sec of 2537-Å radiation. Ultraviolet absorption spectra were monitored with a Cary Model 14 spectrophotometer. Aliquots from irradiated cells were analyzed by gas chromatography with flame-ionization detection; absorbance of deposits on the cell windows was measured after sweeping with N_2.

Benzene at pressures of 0.05–20 torr in 1 atm of N_2 was irradiated at 1849 Å for varying times. At each pressure, the absorbance at 2350 Å attributable to volatile products reached or approached a maximum value which appeared to be proportional to the amount of benzene in the cell. Samples irradiated to the maximum absorbance contained 4–5% fulvene and about 2% each of *cis*- and *trans*-1,3-hexadien-5-yne. The photoproducts were identified as *cis*- and *trans*-1,3-hexadien-5-yne by the correspondence of their gas-chromatographic retentions, uv spectra, and photochemical behavior with those of authentic samples.[7] Their retentions on a variety of columns are shown, together with those of fulvene, in Table I. In pentane solution, each exhibited a uv maximum at 2520 Å, log ε 4.4, and was converted (Φ ∼ 0.1) to its stereoisomer without formation of other monomeric products upon irradiation at 2537 Å. The vapor-phase uv spectra of the hexadienynes show maxima at 2400 Å, close to that previously deduced[5] for a then unidentified photoproduct.

Table I. Gas Chromatographic Retentions of Photoisomers Relative to Benzene

Column[a]	Temp, °C	Fulvene	1,3-Hexadien-5-yne *cis*	1,3-Hexadien-5-yne *trans*
Apiezon L	50	0.80	0.65	0.87
Didecyl phthalate	23	0.83	1.06	1.20
Tri-*o*-tolyl phosphate	23	0.86	1.21	1.34
Carbowax-KOH[b]	50	0.95	1.79	2.03

[a] Chromosorb G support. [b] 5% Carbowax-750, 2% KOH.

To investigate their origin, the distribution of products in the photolysis of 20 torr of benzene in 1 atm of N_2 was studied as a function of time. Expressed as per cent of benzene, yields of fulvene and *cis*- and *trans*-hexadienyne, respectively, were: 0.10, 0.022, <0.002 after 15 sec; 0.40, 0.075, 0.014 after 1 min; 1.4, 0.29, 0.15 after 5 min; 4.2, 1.2, 1.0 after 20 min. It may be noted that the ratio of *trans*- to *cis*-hexadienyne increases from less than 0.1 to almost unity as photolysis proceeds, and that the ratio of hexadienynes to fulvene increases only from 0.22 to 0.31 while the fulvene concentration increases 14-fold. It can be concluded from these results, and from similar results at lower benzene pressures, that *cis*-1,3-hexadien-5-yne is formed from benzene at about one-fourth the rate of fulvene formation, and that the *trans* isomer is produced by secondary photolysis.

To aid in understanding later stages of the photolysis, fulvene and *cis*-hexadienyne at pressures *ca.* 0.01 torr in 1 atm of N_2 were irradiated at 1849 Å. *cis*-Hexadienyne isomerized to the *trans* compound and "polymerized" at comparable rates, yielding no other volatile product. Fulvene disappeared at a similar rate ($t_{1/2} \sim 30$ sec) yielding "polymer," benzene, and hexadienyne in a ratio of 2:1:1. The photolysis rates are consistent with the observed limiting concentrations of fulvene

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 3698 (1966).

[3] K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

[4] H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 162 (1967).

[5] L. Kaplan and K. E. Wilzbach, **89**, 1030 (1967).

[6] J. L. Weeks, S. Gordon, and G. M. A. C. Meaburn, *Nature*, **191**, 1186 (1961).

[7] F. Sondheimer, D. A. Ben-Efraim, and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

and hexadienynes in the benzene photolyses and indicate that at steady state a substantial fraction of hexadienyne is formed from fulvene.

Fulvene and the hexadienynes were also irradiated at 2537 Å under similar conditions, with results which differed markedly from those at 1849 Å or in solution at 2537 Å. In contrast to the behavior of fulvene in solution, where conversion to benzene does not occur[8] upon irradiation at 2537 Å, an almost quantitative yield of benzene was obtained in the vapor phase, $\Phi \sim 0.01$. The hexadienyne vapors exhibited not only the rapid *cis–trans* isomerization observed in solution, but also a slower, $\Phi \sim 0.01$, almost quantitative conversion to a 2:1 mixture of benzene and fulvene. As a consequence of these reactions, lower steady-state concentrations of fulvene, and particularly of hexadienyne, were obtained when benzene was photolyzed without exclusion of 2537-Å radiation.

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[8] H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

[9] Participant in the CSUI-ANL Honors Program, spring 1967.

Book Reviews

Extrusion Reactions. By B. P. Stark, M.A., Ph.D., Chief Research Chemist, CIBA (A.R.L.) Ltd., Duxford, Cambridge, and A. J. Duke, M.A., Ph.D., A.R.I.C., CIBA (A.R.L.) Ltd., Duxford, Cambridge (now Head of Coatings Department, Central Research Laboratories, Richard Thomas and Baldwins Ltd., Whitchurch, Aylesbury, Bucks). Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1967. x + 190 pp. 14 × 22.5 cm. $10.00.

The provocative title of this slim volume derives from a restricted group of the general class of fragmentation reactions. An "extrusion reaction" is defined as one "in which a small inorganic fragment (including carbon monoxide and carbon dioxide) is totally eliminated from a cyclic organic compound to form a (cyclic) product which either has a ring smaller than that present in the starting material (ring contraction) or has a smaller number of fused rings (bridge expulsion or ring degeneration)." Included under this definition are such familiar examples as the decarbonylation and decarboxylation reactions of bicyclic derivatives carrying bridged carbonyl systems to yield cyclohexadienyl and aromatic products, the elimination of nitrogen from pyrazolines to form cyclopropanes, and the decomposition of benzo[*c*]-2,5-dihydrothiophene dioxide to produce benzocyclobutene. Excluded by the restricted definition are reactions which lead to purely acyclic products (*cf.* the stereospecific fragmentations of 3-sulfolenes and diazene derivatives of 3-pyrrolines) or to more than one residual organic fragment.

In the first chapter, the authors introduce a rather elaborate classification system for extrusion reactions based on the structure of the intermediate *residuum*, formally conceived as the diradical or zwitterionic species immediately generated by expulsion of the inorganic moiety. Three general classes and four subclasses are recognized which differ in the kind and degree of internal stabilization available in the system of atoms comprising the residue. While systematics of this sort may appeal to some readers, this reviewer found the classification more distracting than useful.

In the chapters which follow, extrusion reactions are grouped according to the moiety expelled. Carbon monoxide and carbon dioxide extrusions from bridged carbonyl systems are treated in Chapters 2 and 3, other extrusions of carbon oxides in Chapter 4. Further subdivisions of these extrusions are made on the basis of the *residua* classification where appropriate. Extrusions of sulfur dioxide and other oxidized sulfur fragments are reviewed in Chapter 5; succeeding chapters deal with the extrusions of elemental sulfur, selenium, and oxygen. Nitrogen extrusions are treated in a sequence of four chapters and include the well-documented cases of extrusions from pyrazolines and triazolines as well as the possible intermediacy of oxadiazolines and thiadiazolines in the syntheses of oxirans and thiirans by the action of diazo compounds on carbonyl and thiocarbonyl systems. Extrusions of a few miscellaneous fragments, *e.g.*, cyanate ion and "sulfimide" (SO_2NH), and some examples of multiple extrusions are discussed briefly in later chapters. In a final chapter is presented a summary of such generalizations and interrelationships as do emerge from the material surveyed.

This monograph, brief as it is, contains a wealth of information and carries references to the relevant literature through September 1965. The compendium-like style in which it is written makes for rather tiresome reading; and there is little critical evaluation of the material presented. As a source book for the specialist who wishes to explore this somewhat artificially defined area of fragmentation reactions, however, it should prove quite valuable.

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Electrolyte Theory. An Elementary Introduction to a Microscopic Approach. By Pierre M. V. Résibois, Université Libre de Bruxelles. Harper and Row, 49 East 33D St., New York, N. Y. 1968. x + 166 pp. 16 × 24 cm. $11.25.

Changes in the most effective way to teach subjects like electrochemistry are often motivated by continuing progress in the statistical-mechanical theory of liquids. This book nicely illustrates such trends. Professor Résibois offers here a short introduction to some of the fundamental concepts of electrochemical theory in a distinctly modern manner. The text has grown out of a lecture series given by the author to advanced undergraduates, but it seems to be a potentially valuable guide not only to graduate students polarized toward theoretical work, but also to more mature electrochemists who wisely choose to stay abreast of current theoretical thinking.

The book's objective is relatively modest. The author sets out primarily to derive and explain the low-concentration limiting laws for both electrolyte thermodynamic behavior and linear transport properties. He accomplishes this task with erudition, but not arrogance. Although molecular distribution function theory provides the prevalent language, the approximations are honestly displayed and given clear motivation. Furthermore, simple intuitive explanations for the existence of the limiting laws are offered.

A substantial portion of the book is devoted to the theory of Brownian motion. This material is a valuable exposition in its own right, quite apart from electrochemical applications.

The reader might well be warned that the emphasis is on the physical (rather than chemical) aspects of electrochemistry. Nevertheless, it should become clear to anyone who studies this book carefully exactly where in the general theory the distinctively chemical differences between various salts and solvents would have to enter.

One important phenomenon which was not mentioned, but whose inclusion would be pedagogically consistent with the material offered, is ionic retardation due to solvent dielectric relaxation. Unfortunately, this effect (associated over several decades with the