

30 sec) caused complete scrambling⁶ of deuterium between the acetylenic and vinyl positions of **2** and no such rearrangement in the trans isomer **3** (<1% detectable). The cis scrambling reaction is rapid even at temperatures 100° lower; the label is approximately half-equilibrated after 30-sec exposure at 200°. No scrambling in either isomer took place on ultraviolet irradiation ($\lambda > 220$ nm) in either cyclohexane or benzene solution. Repeated exposure of a sample of **2a**, which has been subjected to pyrolysis, to DBN-triethylene glycol (under conditions shown in independent control experiments to completely replace only the acetylenic deuterium in **2** with hydrogen) produced molecules containing only zero and two deuterium atoms (<2.5% d_1 species). This demonstrated that the scrambling reaction interconverts only **2a** and **2b**; no single-exchange products (**2c** and **2d**) are formed. *These data require that 2a is being transformed via an intermediate or transition state 1 in which C-1, C-3, C-4, and C-6 are chemically equivalent.*^{6a}

Compound **2** polymerizes at moderately high concentrations in solution even at 25°. When kept sufficiently dilute, however (<0.01 M), the material can be heated to 200° without extensive decomposition. In hydrocarbon solvent (2,6,10,14-tetramethylpentadecane), a new product, benzene, begins to appear at the expense of **2a**. This suggests that **1**, like the diradical generated on pyrolysis of *p*-cyclophane,⁷ is capable of abstracting hydrogen atoms from a donor solvent. Reaction of **2** in toluene produces diphenylmethane as a major product, and in CCl₄ only 1,4-dichlorobenzene is observed. All these are typical free-radical reactions⁸ and are best understood by assuming that the symmetrical intermediate produced on thermolysis of **2** is the 1,4-benzenediyl diradical **1c**. Even when given a choice of behaving as a polar or radical species, the intermediate selects the latter: reaction in methanol at 200° gives mostly benzene and some benzyl alcohol, but no anisole.⁹

From the contact time needed to approximately half rearrange **2a** at 200°, one can estimate that ΔF^\ddagger

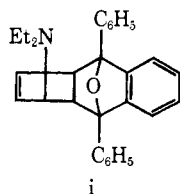
(6) Cis-trans isomerization of **2** becomes detectable only at temperatures ~150° higher than those required for the deuterium scrambling reaction.

(6a) NOTE ADDED IN PROOF. Compound **2** was shown to contain >95% d_2 species both before and after pyrolysis, demonstrating the absence of exchange with adventitious protium on the vessel walls. Further evidence for the unimolecular nature of the **2a** \rightleftharpoons **2b** reaction has been obtained by thermolysis of a sample of partially deuterated **2** containing 44% d_2 , 12% d_1 , and 44% d_0 species. No excess d_1 species (limits of detection, 2%) was found in the pyrolysate. We are grateful to Professor Martin Stiles for suggesting this experiment.

(7) H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3517 (1969).

(8) W. A. Pryor, "Free Radicals," McGraw-Hill, New York N. Y., 1966.

(9) R. Breslow and J. Napierski have prepared 1-chlorobicyclo-[2.2.0]hexa-2,5-diene. On treatment with lithium diethylamide in the presence of diphenylisobenzofuran, compound **i** is produced. IF



p-benzyne is an intermediate in this reaction, it apparently has a different structure when generated under these conditions than it has in the neighborhood of 200°. We are grateful to Professor Breslow for communicating these results to us prior to publication.

($\cong \Delta H^\ddagger$)¹⁰ for the reaction is about 32 kcal/mol. The heat of formation of **2** can be reliably estimated using group equivalent techniques¹¹ to be +126 kcal/mol. This requires that the maximum ΔH_f° possible for **1** is the enthalpy of the transition state leading to it, i.e., +158 kcal/mol. However, ΔH_f° for benzene-1,4-diyl can be estimated¹² by adding two phenyl C-H bond energies (each 112 kcal/mol^{11a}) to ΔH_f° for benzene¹³ (+19.8 kcal/mol) and subtracting the bond energy of H₂. The result is +140 kcal/mol, indicating that ΔH° for the **2** \rightleftharpoons **1c** reaction is only $\cong +14$ kcal/mol. If the activation energy and endothermicity of this reaction are truly so different, **1c** may lie in an appreciable (18 kcal/mol?) unimolecular energy well and may be capable of detection by spectroscopic techniques, especially if it has a triplet ground state.^{2b} Attempts at such detection are under way.

Acknowledgments. We are grateful for financial support of this work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

(10) Because no free rotational modes need to be frozen out in the transition state leading from **2** to **1**, the activation entropy (ΔS^\ddagger) is undoubtedly very close to zero for this reaction.^{11a} Kinetic studies are being carried out to verify this assumption.

(11) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(12) For a discussion of estimates of the heats of formation of other diradicals, and the assumptions involved, see (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970); (c) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963).

(13) N. S. Osborne and D. C. Ginnings, *J. Res. Nat. Bur. Stand.*, **39**, 453 (1947).

(14) (a) National Science Foundation Predoctoral Fellow, 1969-1971; (b) Alfred P. Sloan Foundation Fellow, 1970-1972; Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970-1975.

Richard R. Jones,^{14a} Robert G. Bergman^{*14b}

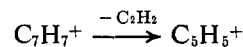
*Contribution No. 4366, Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109*

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Structure and Reactivity of Organic Ions in Gas-Phase Radiolysis. V. The Structure and Formation Process of the C₇H₇⁺ Ion from Toluene¹

Sir:

The structure of the abundant C₇H₇⁺ ion derived from toluene and higher alkylbenzenes has attracted a great deal of research interest in the field of mass spectrometry as well as that from other C₇H₈ isomers including cycloheptatriene, and considerable evidence has accumulated which demonstrates that the C₇H₇⁺ ion is not a benzyl ion but a symmetrical tropylium ion.^{2,3} Much of this evidence has been obtained from the isotope labeling studies on the decomposition process



For toluene, the isotope retentions in the C₇H₇⁺ ions from deuterated toluenes indicate that the eight hydro-

(1) For paper IV, see S. Takamuku, K. Nakamura, and H. Sakurai *Bull. Chem. Soc. Jap.*, in press.

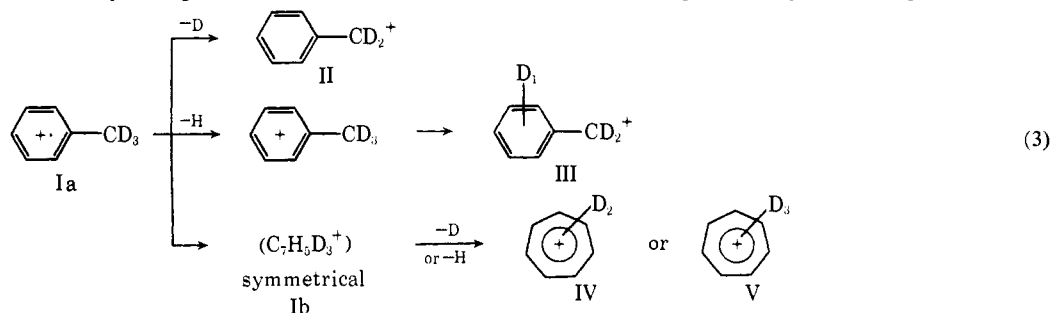
(2) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 453.

(3) A recent study is, for example, A. S. Siegel, *J. Amer. Chem. Soc.*, **92**, 5277 (1970).

gen atoms are almost completely scrambled in the molecular ion, and Meyerson has concluded that toluene molecular ions rearrange to a cycloheptatriene-like structure.⁴ Furthermore, the scrambling of hydrogen atoms has recently been studied as a function of the internal energy of the molecular ion in the mass spectrometry of deuterated toluenes and cycloheptatrienes by Howe and McLafferty.⁵ It has been reported that the degree of scrambling decreases with increasing internal energy, and hence in the case of toluene some part of the $C_7H_7^+$ ion yield is formed by the direct dissociation of α hydrogen before the scrambling of the hydrogen atoms occurs.⁶

On the other hand, during the course of our investigation of the gas-phase radiolysis it has been found that the $C_7H_7^+$ ion from toluene, ethylbenzene, *m*-xylene,⁷ and cycloheptatriene reacts with aromatics to produce benzylated products, and this reaction has been regarded as an electrophilic substitution reaction, which is well known in solution chemistry.^{1,8-11} Such a reactivity of the $C_7H_7^+$ ion with aromatics as well as the structure of the products seemed to suggest that the $C_7H_7^+$ ion from these compounds in the gas-phase radiolysis is a benzyl ion having a positively charged center rather than a tropylium ion in which the positive charge is distributed equally among the seven carbon atoms. However, there is still the possibility of the rearrangement of the $C_7H_7^+$ ion from a tropylium structure to a benzyl one. Such a possibility is of interest in connection with the question of the structure of the primarily formed $C_7H_7^+$ ion.

In the gas-phase radiolysis of toluene, three isomers of methyl diphenylmethane (MDPM) are formed by the reaction of the $C_7H_7^+$ ion with the parent molecule as in eq 1 and 2.^{8,9,11} In the present investigation using toluene- α - d_3 , the isotope distribution in the produced MDPM's has been determined by using nmr and mass



spectra in order to obtain information about the structure and formation process of the $C_7H_7^+$ ion in the gas-phase radiolysis of toluene.

(4) S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963).

(5) I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971). The role of internal energy in determining the extent of hydrogen scrambling in the $C_7H_7^+$ ion from benzyl compounds has also been discussed in S. Meyerson, H. Hart, and L. C. Leitch, *ibid.*, **90**, 3419 (1968).

(6) The "direct dissociation" process was first proposed in order to interpret the slight preferential loss of H or D from the methyl group in the mass spectra of deuterated toluenes (J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964)).

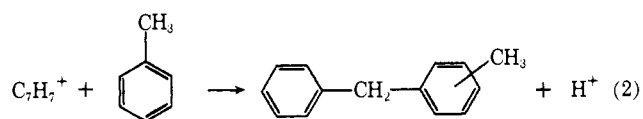
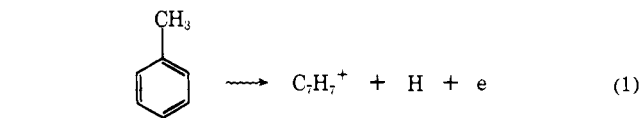
(7) The same reaction of the $C_7H_7^+$ ion from other xylene isomers has also been observed and the result is to be published.

(8) Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

(9) Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, **74**, 3325 (1970).

(10) Y. Yamamoto, S. Takamuku, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **44**, 574 (1971).

(11) Y. Yamamoto, S. Takamuku, and H. Sakurai, *ibid.*, **44**, 2104 (1971).



The toluene- α - d_3 vapor was irradiated with 3000 Ci of ^{60}Co γ rays at a pressure of about 19 mm and at room temperature.¹² The produced MDPM's were separated from the reactant and other products by a preparative gas chromatography, and submitted to nmr spectrometry. The ratio of the methylene and phenyl protiums of the MDPM's was determined to be 0.062 from the nmr spectrum.¹³ The mass spectrum of the MDPM's showed that MDPM- d_5 and - d_6 are formed in the ratio of 1.4, which indicates the ratio of the $C_7H_5D_2^+$ and $C_7H_4D_3^+$ ions producing the MDPM's.¹⁴ This ratio is larger than that in the mass spectrum of toluene- α - d_3 .² From these mass and nmr spectra, the ratio of the methylene and phenyl protiums of the benzyl groups of the MDPM's, H_{CH_2}/H_{Ph} , was calculated to be 0.12. If the $C_7H_5D_2^+$ and $C_7H_4D_3^+$ ions took a tropylium structure, the protium and deuterium atoms of the benzyl groups of the MDPM's would be statistically distributed between the methylene and phenyl units, and the H_{CH_2}/H_{Ph} ratio would be 0.40. On the other hand, if these ions were the benzyl ions retaining the original toluene- α - d_3 structure, no protium atom would be introduced to the methylene groups of the MDPM's. The observed H_{CH_2}/H_{Ph} ratio is in large excess of that expected from the isotopic impurity of the toluene- α - d_3 in the latter case, and indicates that a partial isotope scrambling occurs in the precursor ions of the MDPM's.

The result can be explained by assuming the forma-

tion and reaction of the $C_7H_7^+$ ions from toluene- α - d_3 as in eq 3. The benzyl ions, II and III, are formed by the direct dissociations of D and H from the molecular ion, Ia, respectively, the latter of which is followed by the D⁻ transfer from the methyl to the phenyl group.¹⁵ These

(12) Toluene- α - d_3 was prepared by the method given in the literature (R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956)), and the deuterium content of the methyl group was 93.5%, determined by a nmr spectrum. Irradiation was carried out in a 6-l. Pyrex flask for 2 weeks. Any radical scavenger was not added, since MDPM's are exclusively formed by the ionic reaction (see ref 8 and 9).

(13) Nmr spectrum of the MDPM's was obtained with a Hitachi Perkin-Elmer R-20 spectrometer as a solution in carbon tetrachloride with TMS as the internal standard. The feature of the spectrum was H_{Ph} , τ 1.9-2.1; H_{CH_2} , τ 5.1; and H_{CH_3} , τ 6.8. The H_{CH_3} signal was attributable to the isotopic impurity of the toluene- α - d_3 .

(14) The mass spectrum was determined with a directly coupled gas chromatograph-mass spectrometer (Hitachi RMS-4 mass spectrometer).

(15) The benzyl ion, II, might be also formed by the D⁻ transfer from toluene- α - d_3 to any primary ion involving the $C_7H_7^+$ ion. However, the contribution of such a secondary ion to the MDPM's forma-

ions rapidly react with the toluene- α - d_3 molecules to produce MDPM's before the isomerization to tropylium ions occurs. On the other hand, the tropylium ions, IV and V, are formed by the loss of D and H, respectively, *via* the symmetrical intermediate, Ib, as previously proposed by Meyerson.⁴ These tropylium ions also produce the MDPM's, in which the deuterium atoms are statistically distributed in the benzyl groups, *via* the isomerization of a tropylium structure to a benzyl one.

The benzyl ions, II and III, produce the MDPM's having five and four H_{Ph} , respectively, and no H_{CH_2} in the benzyl group. When i represents the isotope effect (k_H/k_D) on the hydrogen loss from the symmetrical intermediate Ib, the ratio of IV/V is $3/5i$, and the numbers of H_{Ph} and H_{CH_2} in the benzyl group of the MDPM's produced from these ions are given by $5[(5 \times 3) + (4 \times 5i)]/7(5i + 3)$ and $2[(5 \times 3) + (4 \times 5i)]/7(5i + 3)$, respectively. On the other hand, the numbers of H_{Ph} and H_{CH_2} in the benzyl group of the MDPM's produced in the gas-phase radiolysis of toluene- α - d_3 were calculated to be 4.1 and 0.5, respectively, from the nmr and mass spectra. Thus, on the assumption of the wide range of i , 1-4,¹⁶ the relative contributions of II, III, and IV and V to the MDPM's formation were calculated to be 30-37, 39-29%, and 31-33%, respectively, by correcting for the deuterium content of the toluene- α - d_3 .¹⁷ It may be concluded that in the gas-phase radiolysis of toluene only about one-third of the $C_7H_7^+$ ion leading to the formation of MDPM's is formed through the symmetrical intermediate, Ib. On the basis of the previous study of Howe and McLafferty,⁵ the observed discrepancy between the gas-phase radiolysis and the mass spectrometry may be explained in terms of the internal energy of the molecular ion; the molecular ions having certain internal energies play important roles in the gas-phase radiolysis and produce benzyl ions before a ring expansion, and the produced benzyl ions rapidly react with toluene molecules to produce MDPM's.¹⁸ Further studies of the reactions and formation process of the $C_7H_7^+$ ion from toluene and higher alkylbenzenes will be discussed in full papers.

Acknowledgment. We wish to thank Dr. Seung-Geon Kim for advice on the preparation of toluene- α - d_3 . Thanks are also due to Yoshio Takai for assistance in the measurement of nmr spectra.

tion may be considered to be much smaller than that of the primary $C_7H_7^+$ ion, since in the gas-phase radiolysis of ethylbenzene and xylenes the C_{16} products, expected to be formed by the reactions of the analogous secondary ions, $C_6H_5C^+HCH_3$ and $CH_3C_6H_4CH_2^+$, respectively, were formed with much smaller yields than those of the benzylated products.

(16) This range of the isotope effect seems to be reasonable, since it has been reported by Howe and McLafferty that this isotope effect is 2.8 when the complete isotope scrambling occurs (see ref 5).

(17) In correcting for the deuterium content of the toluene- α - d_3 , the isotope effects on the direct dissociation producing II and on the intramolecular hydride ion transfer producing III were neglected, although these isotope effects somewhat affect the calculated values.

(18) Evidence has been reported which demonstrates that some part of the isotope-scrambled $C_7H_7^+$ ion produces toluene (K. E. Wilzbach, presented before the International Atomic Energy Agency Conference, Copenhagen, Denmark, Sept 1960), although in this study no information about the $C_7H_7^+$ ion producing the products other than MDPM's was obtained.

Yukko Yamamoto,* Setsuo Takamuku, Hiroshi Sakurai
The Institute of Scientific and Industrial Research
Osaka University, Suita, Osaka, Japan

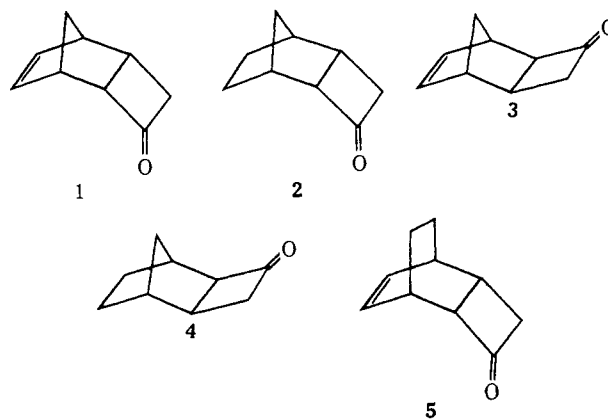
Received October 9, 1971

Stereoselectivity in the Photochemical Cycloelimination of Some Polycyclic Cyclobutanones

Sir:

The solution photochemistry of cyclobutanones has been characterized by three primary processes: (1) fragmentation (cycloelimination) into ketenes and olefins, (2) decarbonylation, and (3) ring expansion to yield cyclic acetals in alcoholic solvents.¹ The cycloelimination and ring expansion reactions, which may proceed *via* a common precursor, show remarkable stereoselectivity which is accurately predicted by cleavage to generate the most stable radical pair.¹⁻³ Unfortunately, the selectivity of the cycloelimination, while mechanistically interesting, is often of limited synthetic potential, representing in many cases merely a reversal of the original synthesis.

The incorporation of a strained cyclic moiety, whose additional strain contribution could be removed *via* cycloelimination, into a 2,3-cis fused polycyclic cyclobutanone should repress the elimination of ketene and lead ultimately to synthetically useful products conveniently described in terms of initial cleavage to the less stable of the possible acyl-alkyl radical pairs. To test this hypothesis the photochemistry of the tricyclic ketones 1-5⁴ was examined.



The irradiation (3000 Å, 35°) of a degassed solution of 1 (0.02 M) in pentane resulted in the rapid disappearance of starting material and the appearance of a single major product (48-52%) together with small amounts of norbornadiene (<1%).⁵ The photo-product reacted rapidly upon addition of methanol to quantitatively produce a methyl ester (mol wt 166) assigned structure 6. This structural assignment rests firmly on analytical and spectral data. The ir spectrum of 6 showed strong bands at ν^{film} 3000, 2900, 2800, 1740, 1635, 1260, 1190, 1160, 1020, 995, and 920 (monosubstituted olefin) and 750 cm^{-1} (cis double bond). The nmr spectrum had absorbances at τ^{CDCl_3} 3.93-

(1) (a) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968); (b) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970), and references cited therein.

(2) (a) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970); (b) N. J. Turro and D. R. Morton, *ibid.*, **93**, 2569 (1971).

(3) The anomalous effect of a strained trans-fused cyclobutanone on the stereoselectivity of the photochemical ring expansion (although *not* cycloelimination) has been reported previously by Quinkert and co-workers: G. Quinkert, G. Cimbollek, and G. Buhr, *Tetrahedron Lett.*, 4573 (1966).

(4) The synthesis and properties of these and other polycyclic cyclobutanones will be described elsewhere.

(5) All of the cyclobutanones examined, 1-5, produced some of the corresponding decarbonylated hydrocarbon in low yield (<2%).