

ever, that only a zero-flip rearrangement (in which the six Mo-NC₂ planes rotate through b) and a fluxional process involving a concerted pairwise exchange of dimethylamido ligands allow molybdenum to retain an 18-electron valence shell throughout.

We are currently extending our studies to the synthesis and characterization¹⁴ of the series Mo₂L₆ where L = Ar, PR₂, and SR.

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(14) Single-crystal X-ray diffraction studies are being carried out on Mo₂(O-*t*-Bu)₆, Mo₂(NMe₂)₆, and related compounds by Professor F. A. Cotton and coworkers.

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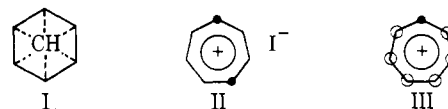
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Rearrangement Ions. V.¹ The C₇H₇⁺ Ion in the Mass Spectrum of Tropylium-1,4-¹³C₂ Iodide

Sir:

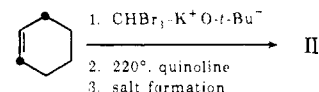
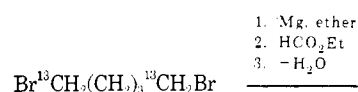
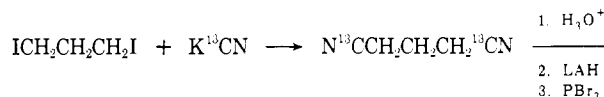
Since Meyerson's earlier discovery that the hydrogen atoms in toluene attain almost complete equivalence in the process leading to the formation of C₇H₇⁺ ions,² several efforts have been directed at examining the electron impact induced skeletal reorganization of toluene and related benzyl systems utilizing ¹³C labeling.³⁻⁵ Thus, a single ¹³C atom in position α,^{2,3} 1,^{3,5} or 2⁴ is nearly lost statistically in the path C₇H₇⁺ → C₅H₅⁺. These results support, although do not prove, Meyerson's original proposal of a tropylium ion structure for the C₇H₇⁺ ion. Whereas a single ¹³C atom may distinguish between a benzyl ion and a tropylium ion structure for the fragmenting C₇H₇⁺ ion, it cannot offer information regarding the mode of formation of the C₇H₇⁺ ion. Rinehart, *et al.*,^{3,5} in examining toluene-α,¹-¹³C₂ found that the label retentions in the C₅H₅⁺ ions indicated that the C₇H₇⁺ ions are not formed solely, if at all, by insertion of the α-carbon atom between C₁ and C₂ of the ring, but rather by a mechanism in which some or all of the carbon atoms have lost positional identity with respect to their toluene origin, *e.g.*, by insertion of the α-carbon atom randomly between adjacent carbon atoms of the ring (I).⁶ A subsequent report⁴ dealing with the mass spectrum of toluene-2,6-¹³C₂, a doubly labeled toluene in which the ¹³C atoms are not adjacent, showed that some unlabeled C₅H₅⁺ ions and some ¹³C₂-H₂⁺ ions were formed. These data suggested a mechanism more complicated than I.

In order to gain more insight into the problem, efforts were directed at examining the mass spectrum of tro-



pylium-1,4-¹³C₂ iodide (II) in order to determine whether scrambling occurs in those C₇H₇⁺ ions which have sufficient energy to form C₅H₅⁺ ions. Synthesis of II proceeded according to Scheme I,⁷ which represents

Scheme I



only minor modifications of procedures described.⁸⁻¹⁰ Mass spectra were recorded on an AEI MS-9 mass spectrometer at a resolution of 16,000 (10% valley definition); data represent averages of 15-20 scans.

Loss of C₂H₂ from a skeletally "intact" C₇H₇⁺ ion derived from II should produce no unlabeled C₅H₅⁺ ions; loss of C₂H₂ from a skeletally rearranged C₇H₇⁺ ion (III) should produce some unlabeled C₅H₅⁺ ions, the precise amount depending on the extent and mode of reorganization. The anticipated relative abundances, as well as the observed data recorded at 70 and 20 eV, are presented in Table I.

Table I. High Resolution Mass Spectral Peaks

| m/e | Composition ^a | Relative abundance ^{b-d} | | | |
|-----|--|-----------------------------------|-------|------------|-------------------------|
| | | 70 eV | 20 eV | Theory II' | Theory III ^e |
| 65 | C ₅ H ₅ ⁺ | 0.029 | 0.039 | 0.000 | 0.048 |
| 66 | ¹³ CC ₄ H ₅ | 0.549 | 0.500 | 0.571 | 0.476 |
| 67 | ¹³ C ₂ C ₃ H ₅ | 0.422 | 0.461 | 0.429 | 0.476 |

^a Other hydrocarbon ions omitted. ^b Σ65-67 = 1.000 ^c Corrected for naturally abundant ¹³C. ^d Calculated for 100% isotopic enrichment. ^e Sample contained 83.5% doubly labeled, 15.7% singly labeled, and 0.8% unlabeled tropylium iodide. ^f Calculated for unrearranged II. ^g Calculated for a completely scrambled ion (III).

The presence of unlabeled C₅H₅⁺ ions, as well as ¹³C₂H₂ ions beyond that of natural abundance, suggests extensive skeletal reorganization. As anticipated, the extent of reorganization increases at lower ionizing

(7) The disposition of the labels in the cyclohexene was substantiated by comparison of its mass spectrum with cyclohexene and cyclohexene-1-¹³C. Prior nmr evidence (see ref 6) showed no skeletal rearrangement in the dehydration of labeled methylcyclohexanol. The synthesis of several dimethyl-, methylethyl-, and diethyltropylium salts from the appropriate alkyl cyclohexenes by the method described in Scheme I afforded the expected tropylium salts indicating no skeletal rearrangement.

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(1) For paper IV, see A. Siegel, *Tetrahedron Lett.*, 4113 (1970).

(2) H. M. Grubb and S. Meyerson in "Mass Spectra of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

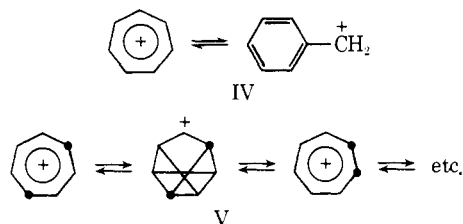
(3) K. L. Rinehart, Jr., A. C. Buchholz, G. E. VanLear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

(4) A. Siegel, *J. Amer. Chem. Soc.*, **92**, 5277 (1970).

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(6) A. C. Buchholz, *Diss. Abstr. B*, **28**, 3215 (1968).

voltages.¹¹ A recent report¹² dealing with the mass spectra of tropylium salts has indicated that the appearance potentials of the $C_7H_7^+$ ions derived from tropylium iodide, bromide, and tetrafluoroborate are identical (6.74 eV), close to the spectroscopic ionization potential of the cycloheptatrienyl radical (6.24 eV), and very close to the electron impact value for the cycloheptatrienyl radical (6.60 eV). This suggests that prior to vaporization, the tropylium ion undergoes a "one-electron reduction" to the radical followed by ionization to the $C_7H_7^+$ ion, presumably the tropylium ion. Hence, either the tropylium ion or the cycloheptatrienyl radical or both is undergoing skeletal reorganization prior to the formation of $C_5H_5^+$ ions, perhaps *via* a series of benzyl ion-tropylium ion isomerizations (IV) or *via* a series of valence tautomeric shifts (V). The



observed data imply that the near total loss of positional identity of the carbon atoms in toluene may not occur solely, if at all, in the process leading to the formation of $C_7H_7^+$ ions, but rather after its formation. Further studies on II including other ions in the spectrum will be discussed later.

Acknowledgment is made to the Indiana State University Research Fund Committee for their support of this work and to Mr. J. Boal of the Mellon Institute for running the spectra.

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(12) G. Hvistendahl, K. Undheim, and P. Gyrosi, *Org. Mass Spectrom.*, 7, 903 (1973).

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On the Stereoselectivity and Regiospecificity of Spiroannulations with 1-Lithiocyclopropyl Phenyl Sulfide

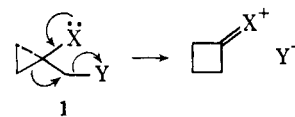
Sir:

The directed ring expansion of cyclopropylcarbinyl systems to cyclobutyl systems has shown much promise in synthetic organic chemistry.¹⁻³ In this communication we wish to show for **1** ($X = PhS$) that (1) the re-

(1) C. R. Johnson, *Accounts Chem. Res.*, 6, 341 (1973); H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, 91, 2376 (1969); H. H. Wasserman, H. W. Adikes, and O. E. de Ochoa, *ibid.*, 93, 5586 (1971); J. R. Salaun and J. M. Conia, *Tetrahedron Lett.*, 2849 (1972); J. P. Barnier, B. Garnier, C. Girard, J. M. Denis, J. Salaun, and J. M. Conia, *ibid.*, 1747 (1973); E. Wenkert, R. A. Mueller, E. J. Reardon, S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Amer. Chem. Soc.*, 92, 7428 (1970); W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *ibid.*, 93, 657 (1971).

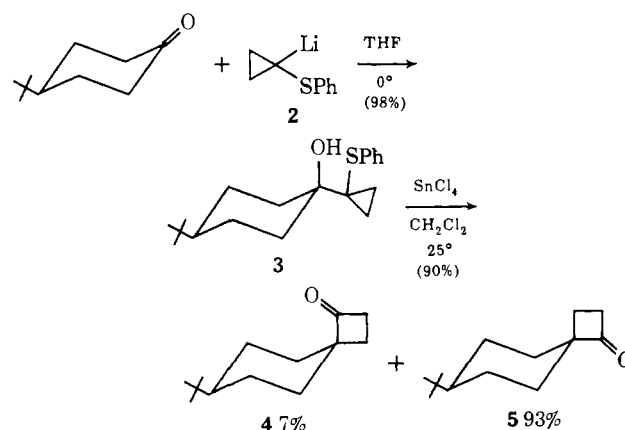
(2) (a) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 93, 3773 (1971); (b) M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, 887 (1972); (c) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 95, 289 (1973); (d) B. M. Trost and M. J. Bogdanowicz, *ibid.*, 95, 5311, 5321 (1973).

(3) B. M. Trost, D. Keeley, and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 95, 3068 (1973).



actions involve carbonium ions and are nonstereoselective, (2) the reactions are nonetheless highly stereoselective, (3) migrations to cyclohexyl carbon involve formation of an axial bond, and (4) electronic not steric factors control the regiospecificity in the case of spiroannulations with enones. These results have special significance in light of their synthetic consequences¹⁻³ and their comparison to the behavior of cyclopropylcarbinyl systems not possessing such directing groups.⁴

Reaction of the organolithium **2** with 4-*tert*-butylcyclohexanone produces an adduct as a 99:1 mixture of two isomers.^{5,6} By analogy to organometallic additions to this ketone,⁷ the major product was assigned the stereochemistry depicted in **3**. Treatment with 1 equiv of anhydrous stannic chloride followed by hydrolysis produces primarily cyclobutanone **5**.² Obtention of the



product requiring retention of configuration at the migration terminus strongly suggests a carbonium ion intermediate rather than a migration concerted with loss of the leaving group. Consideration of the stability of the intermediates allows a rationalization of the delightfully high stereoselectivity seen. Cyclopropylcarbinyl cations assume the bisected geometry (**6**) as the preferred conformation. Migration by path "b" (equatorial migration) swings the phenylthio unit over the top of the cyclohexane ring and thus creates substantial steric crowding. Migration by path "a" (axial migration) swings this unit into a relatively uncrowded region away from the cyclohexane ring. The differential steric crowding favors path "a" which leads to the major observed product. Preferred axial migration contrasts to other intramolecular rearrangements in which the equatorial pathway predominates.^{2,8}

(4) (a) K. Rajeswari and T. S. Sorenson, *J. Amer. Chem. Soc.*, 95, 1239 (1973); (b) M. Julia and Y. Noël, *Bull. Soc. Chim. Fr.*, 3749 (1968).

(5) All new compounds had spectral properties and analytical data in complete accord with the assigned structure.

(6) This analysis was performed by liquid-liquid chromatography on a Corasil II column, flow rate of 2.8 ml/min, hexane solvent.

(7) (a) W. W. Houlihan, *J. Org. Chem.*, 27, 3860 (1962); (b) H. Felkin and C. Frajerman, *Tetrahedron Lett.*, 1045 (1970); (c) H. O. House and W. L. Respess, *J. Org. Chem.*, 30, 301 (1965); (d) J. Moulines and R. Lalonde, *Bull. Soc. Chim. Fr.*, 1075 (1971); (e) C. R. Johnson, C. W. Schroeck, and J. R. Shanklin, *J. Amer. Chem. Soc.*, 95, 7424 (1973), report equatorial to axial attack of 4:1 for phenylthiomethylithium with 4-*tert*-butylcyclohexanone.

(8) For example, see G. Andrews and D. A. Evans, *Tetrahedron Lett.*, 5121 (1972); D. A. Evans and G. C. Andrews, *J. Amer. Chem. Soc.*, 94, 3672 (1972).