phenone was added and the mixture was then flash distilled into a receiver cooled by Dry Ice–trichloroethylene at 80° (8 mm). Glpc analysis on column A of the distillate showed only starting ketone in a 95% recovery.

Reaction of Triphenylphosphine and Sodium Chlorodifluoroacetate Followed by the Addition of Benzaldehyde at 25°.—The ylid was prepared in the usual way under nitrogen by heating a mixture of 31.3 g (0.120 mole) of triphenylphosphine and 18.3 g (0.120 mole) of sodium chlorodifluoroacetate in diglyme for 18 hr at 100°. The deep brown mixture was then cooled to room temperature under nitrogen followed by the addition of 11.0 g (0.104 mole) of benzaldehyde. Continued stirring at 25° for 24 hr yielded, after work-up with *n*-pentane, a 77% recovery of unreacted benzaldehyde and none of the desired 1,1-difluorostyrene.

Reaction of Triphenylphosphine, Sodium Chlorodifluoroacetate, Trifluoroacetophenone, and Tetramethylethylene in Diglyme at 100°.—A mixture consisting of 50 mmoles of triphenylphosphine, 50 mmoles of sodium chlorodifluoroacetate, 50 mmoles of trifluoroacetophenone, and 100 mmoles of tetramethylethylene in 80 ml of diglyme was heated at 100° for 20 hr. Flash distillation of the organic liquids into a receiver cooled by Dry Ice–trichloroethylene followed by glpc on column B showed none of the cyclopropane derivative. The desired 2-phenylpentafluoropropene was obtained in 78% yield.

A control reaction consisting of 100 mmoles of sodium chlorodifluoroacetate and 200 mmoles of tetramethylethylene in 70 ml of diglyme at 100° for 20 hr gave the 1,1-difluorotetramethylcyclopropane in a 12% yield: bp 89.5–90.5° (740 mm, microcapillary), n^{20}_{D} 1.3800. The H^1 nmr spectrum showed only a triplet centered at δ 1.09 (J_{HF} = 2.0 cps). Reported[32] for 1,1-difluoromethylcyclopropane were n^{25}_{D} 1.3772, H^1 nmr triplet at δ 1.08 (J = 2.0 cps).

Anal. Calcd for $C_7H_{12}F_2$: C, 62.69; H, 8.95. Found: C, 62.45; H, 8.61.

Reaction of Triphenylphosphine, Sodium Chlorodifluoroacetate, Trifluoroacetophenone, and Isopropyl Alcohol in Diglyme at 100°.—Isopropyl alcohol was substituted for tetramethylethylene and the reaction was carried out in a similar manner to that previously described. After 70% of the theoretical amount of carbon dioxide had evolved (4 hr) at 100°, the reaction mixture was flash distilled into a receiver cooled by Dry Ice–trichloroethylene. Glpc analysis indicated the absence of the difluoromethylisopropyl ether and the isopropylorthoformate, and showed a 61.4% yield of the 2-phenylpentafluoropropene. In addition to an 84.5% recovery of the isopropyl alcohol, a new peak was observed (10.3% based on starting alcohol).

A control reaction using only isopropyl alcohol (100 mmoles) and sodium chlorodifluoroacetate (50 mmoles) in diglyme at 100° for 8 hr gave a peak with a retention time identical with that of the new peak observed in the former reaction in a 16% yield. A pure sample of this component was obtained by preparative gas chromatography on column D and was found to be the isopropyl ester of chlorodifluoroacetic acid. An authentic sample of this ether was obtained utilizing the method of Bergmann.[43] The isopropyl chlorodifluoroacetate had the following properties: bp 103–104° (742 mm), n^{20}_{D} 1.3616. The infrared spectrum (neat) showed a peak at 5.62 μ (C=O stretch). The H^1 nmr spectrum showed a heptet (relative area 1) centered at δ 5.18 and a doublet centered at 1.35 (relative area 6) for the methyl protons with J_{HH} = 6.0 cps.

Registry No.—1,2-Dichloro-1,1,3,3,3-pentafluoro-2-phenylpropane, 7785-13-9; V, 7781-96-6; VI, 3142-78-7; 1,1-difluorotetramethylcyclopropane, 823-25-6; isopropyl chlorodifluoroacetate, 7781-95-5; 2,4-dinitrophenylhydrazone of trifluoromethylcyclohexyl ketone, 7781-93-3.

Acknowledgment.—The authors wish to thank Dr. P. R. Resnick for his assistance in obtaining the F^{19} nmr spectra. We also thank the National Aeronautics and Space Administration and the National Institutes of Health (GM 11809-03) for providing support for this study.

(43) E. Bergmann, P. Moses, N. Neeman, S. Cohen, A. Kaluszyner, and S. Reuter, *J. Am. Chem. Soc.*, **79**, 4174 (1957).

Mass Spectra of Simple Exocyclic and Endocyclic Olefins

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The mass spectra of several deuterated derivatives of methylcyclohexene and methylenecyclohexane have been obtained and conclusions concerning allylic isomerization, deuterium scrambling, extent of endocyclic–exocyclic double-bond equilibration and fragmentation mechanisms have been formulated.

The use of mass spectrometry in structure elucidation of natural and synthetic materials has been adequately demonstrated,[1] and recently several applications of this technique to simple cyclic and bicyclic terpene hydrocarbons have appeared.[2] While mass spectrometry has been adapted to the quantitative analysis of hydrocarbon types,[3] it was early recognized that extensive structural rearrangement of the carbon skeleton often occurred[4] which invalidated the method for qualitative analytical purposes. Introduction of an olefinic linkage would be expected to provide some fragmentation-direction tendency,[5,6] but sufficient data is given which illustrates the inability of the olefinic linkage alone to direct clean fragmentation in straight-chain olefins.[7] Cyclic olefins might be expected to have a somewhat lessened tendency to isomerize by hydrogen transfer, and Thomas and Willhalm[8] were surprised to observe a significant, approximately equal loss of 43 mass units from both $\Delta^{4(8)}$- and Δ^{3}-menthene (1 and 2,

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(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. I and II, Holden-Day, Inc., San Francisco, Calif., 1964.

(2) (a) R. I. Reed, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 13; (b) E. von Sydow, *Acta Chem. Scand.*, **17**, 2504 (1963); (c) E. von Sydow, *ibid.*, **18**, 1791 (1964); (d) B. Willhalm, A. F. Thomas, and M. Stoll, *ibid.*, **18**, 1573 (1964).

(3) R. A. Brown, *Am. Soc. Testing Mater., Spec. Tech. Publ.*, **389**, 68 (1965).

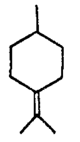
(4) (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957; (b) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p 262.

(5) (a) See F. W. McLafferty [in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 7] for a discussion of fragmentation theory. (b) R. A. Brown and E. Gillams, ASTM E-14 Committee on Mass Spectrometry, New Orleans, La., 1954.

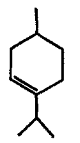
(6) Recently, H. D. Beckey and P. Schulze [*Z. Naturforsch.*, **20a**, 1335 (1965)] have applied the techniques of field ionization to olefins and note that the spectra show features due to the stable configuration of the allyl radical and/or the allyl ion.

(7) (a) R. Ryhage and E. Stenhagen, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 9; (b) R. I. Reed, "Ion Production by Electron Impact," Academic Press Inc., New York, N. Y., 1962, Chapter X; (c) J. A. McCloskey and M. J. McClelland, *J. Am. Chem. Soc.*, **87**, 5090 (1965).

(8) A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, **47**, 475 (1964).



1

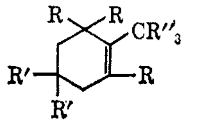


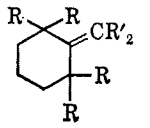
2

respectively). In a paper which appeared[9] after our own work was complete, Weinberg and Djerassi, on the basis of mass shifts observed in two deuterated derivatives of $\Delta^{4(8)}$-menthene, have invalidated the mechanistic explanations proposed by Thomas and Willhalm. A fragmentation mechanism consistent with the new data involved double-bond isomerization prior to fragmentation.

Results and Discussion

Our initial experiments, which showed that the fragmentation patterns of 4-methylcyclohexene and (especially 3-methylcyclohexene were extremely similar to that of 1-methylcyclohexene, led us to study the deuterated derivatives **4**–**6** and **8**–**9** in order to establish the degree of isomerization and hydrogen scrambling in **3** and **7**. The results not only substantiate the proposals of Weinberg and Djerassi, but also provide some information about the relative ease of endocyclic–exocyclic olefin isomerization in free cationic species.





3, R = R' = R'' = H
4, R = R' = H; R'' = D
5, R = D; R' = R'' = H
6, R = R'' = H; R' = D

7, R = R' = H
8, R = H; R' = D
9, R = D; R' = H

Synthesis.—The labeled compounds **4**, **5**, **6**, and **8** were prepared in a high state of isotopic purity by conventional methods. The synthesis of **9** is of more general interest. Atkinson, *et al.*,[10] have reported that use of either α-deuterated carbonyl compounds or α-deuterated phosphonium salts in the methylsulfinyl carbanion dimethyl sulfoxide modification of the Wittig reaction[11] results in extensive loss of the isotope before condensation. Since the Corey modification is a great improvement on the conventional ether system, these results were disappointing. We repeated the condensation of 2,2,6,6-d_4-cyclohexanone (90% d_4) with triphenylphosphinemethylene using equimolar amounts of reactants and obtained methylenecyclohexane with an isotope distribution of 9.7% d_0, 10.1% d_1, 13.7% d_2, 21.8% d_3, 31.8% d_4, and 12.7% d_5 as determined by mass spectrometry. Certainly one method of suppressing this loss of label is to use d_6-methyl sulfoxide,[9] a rather expensive solvent. However, we found that the use of a twice molar excess of the phosphonium salt (with equimolar amounts of sodium hydride and ketone) in the preparation of the ylide resulted in an 89% yield of 90% d_4 olefin (starting with 90% d_4 ketone). Apparently the exchange of α hydrogen occurs *via* an enolization caused by excess dimethylsulfinyl carbanion. This technique is being investigated further.

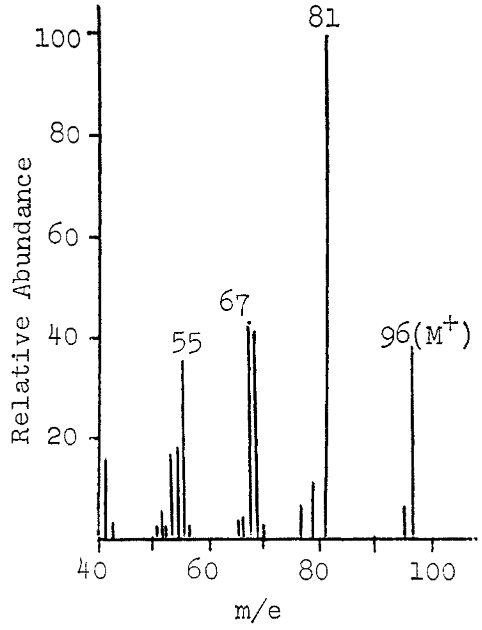


Figure 1.—Mass spectrum of 1-methylcyclohexene.

Mass Spectra. A. Methylcyclohexenes.—In Table I are listed all the important ions in the spectra of the compounds investigated. The spectrum of 1-methylcyclohexene is shown in Figure 1. The base peak of 1-methylcyclohexene, *m/e* 81 (M-CH_3), amounts to 25% of the total ion intensity above *m/e* 39. In the spectrum of **4**, the loss of methyl results in the formation of two ions at *m/e* 81 and 84 (28% total ions). Clearly, only 60% of the methyl loss is due to loss of the substituent; the other 40% is derived from an internal carbon atom. The lack of ions at *m/e* 82 or 83 proves that no extensive hydrogen migrations from the methyl substituent occurred before this fragmentation. In **5** and **6** the loss of the methyl *substituent* is again the dominant constituent of the M-methyl region. Reasonable sources of the nonsubstituent methyl group based on mass shifts in **5** and **6** will be discussed below. It was found[9] that the loss of a methyl group from **1** cannot involve loss of C-3 or C-5, cannot occur to an extent greater than 18% from any of the ring carbons, and need not occur from a ring carbon at all. In fact 82% of the methyl group loss is from the isopropenyl methyls.

One of the several ions in the spectrum of **3** for which the data demand allylic isomerization is *m/e* 68 (10% of total ions), formed by loss of ethylene from the molecule ion *via* a reverse Diels–Alder reaction[12] (m_c^* for 96 → 68 = 48.2; m_f^* = 48.3). Since in the spectrum of 2,6,6-d_3-methylcyclohexene (**5**) approximately 53% of the *m/e* 68 shifts to *m/e* 71 and in the spectrum of 4,4-d_2-methylcyclohexene (**6**) approximately 28% of *m/e* 68 shifts to *m/e* 70, (with the appropriate shift in metastable ion position) the Δ^1 and Δ^2 isomers (a and b, respectively; Scheme I) are contributing to this loss in a ratio of approximately 2:1.

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[9] D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

[10] J. Atkinson, M. Fisher, D. Harley, H. Morse, R. Stuart, and E. Synnes, *Can. J. Chem.*, **43**, 1614 (1964).

[11] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[12] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., New York, N. Y., 1962, p 77.

SCHEME I

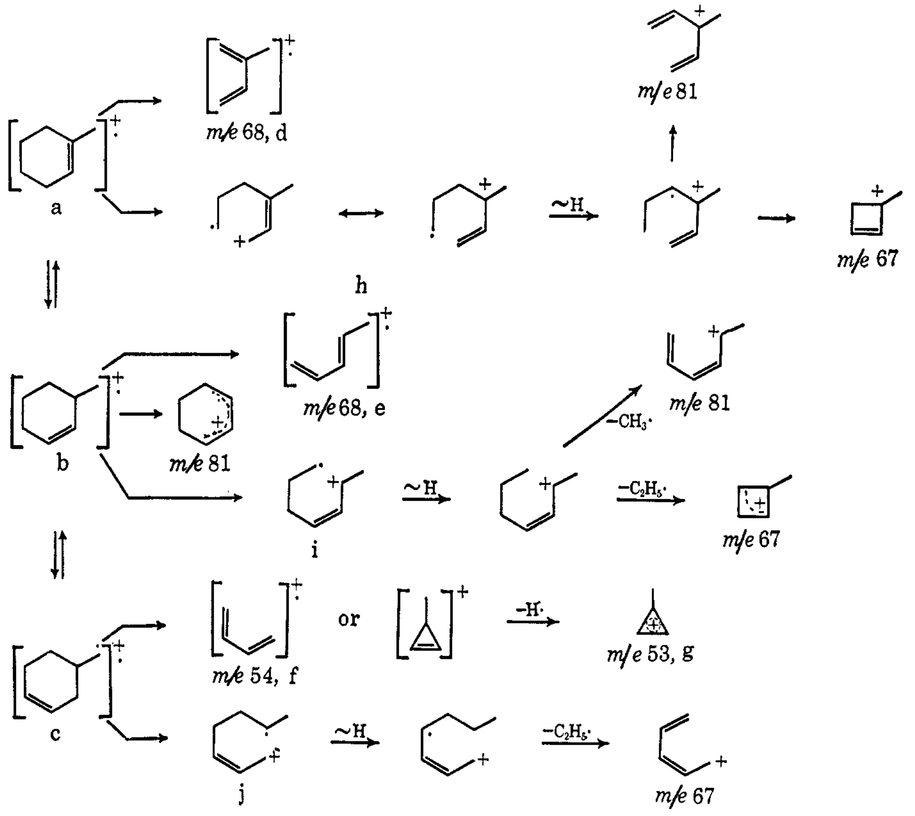
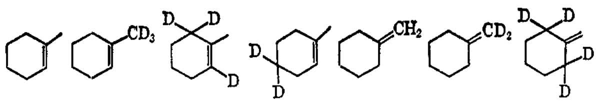


TABLE I
IMPORTANT IONS[a] IN THE MASS SPECTRA OF THE LABELED OLEFINS



m/e	3	4	5	6	7	8	9
100							7.0
99		10.6	8.8				1.5
98		2.8	2.7	8.5		8.2	
97				1.2		1.0	
96	10.7				9.2		
95	1.4				1.0		
85							4.3
84		11.2	16.0				10.8
83			8.5	23.2		8.8	3.2
82			3.0	3.2		1.9	1.3
81	24.3	17.4	1.4	2.2	19.5	10.0	
71		10.2	5.1				3.0
70		5.7	6.3	3.0		6.9	4.6
69		2.2	7.4	6.5		5.7	7.6
68	10.1	1.2	3.1	7.9	10.5	5.0	8.1
67	10.7	4.9		3.7	17.5	9.4	4.1
58		8.3	3.4				1.6
57			4.7	1.1		6.0	3.8
56			4.5	4.4		5.0	4.9
55	8.7	2.5	4.4	6.7	9.2	5.0	7.0
54	4.8	5.7	2.7	2.2	10.5	6.3	5.4
53	4.3	2.0		2.8	3.7	1.6	2.2
43		2.2	5.6			1.9	1.6
42		2.8	2.2	2.5		3.1	2.7
41	4.0	3.7	2.2	2.9	5.7	3.8	3.5

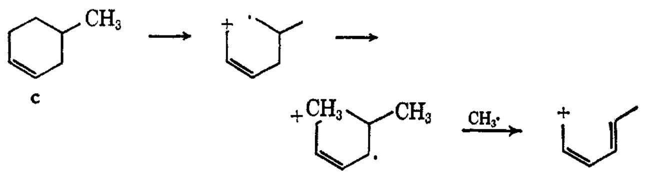
[a] Intensity expressed as per cent of total ions above m/e 39.

The Δ^3 isomer (c) would also be expected to undergo this retro Diels–Alder reaction to produce a butadiene radical cation (f) which has lost the original methyl substituent. This is consistent with the observation that the spectrum of the CD_3 compound 4 exhibits an m/e 54 peak but no m/e 57 peak. Further loss of a hydrogen atom from f produces g, a process in agreement with the observation of (a) a metastable ion at 52.0 ($m_c^* = 52.0$) and (b) a rapid decrease in the relative intensity of the m/e 53 ion at lowered electron energies.

Again, all three isomeric radical molecule ions are important contributors to the m/e 67 ion formed by loss of an ethyl radical. A reasonable route to this ion would incorporate an allylic cleavage followed by a hydrogen atom transfer to form the ethyl group and subsequent loss of this ethyl radical. In Scheme I are outlined possible pathways from each of the molecule radical ions. These particular allylic cleavages in a and b are suggested as major fragmentation routes based on their general consistency (and other pathways' inconsistencies) with the data for the deuterated compounds, although the probability of other pathways are considered later. The cleavages shown in Scheme I also result in the formation of the more stable of alternate carbonium ions.

The spectra of deuterated derivatives indicate that approximately 42% of the total ethyl loss is from the Δ^3 isomer c (from the intensity of m/e 67 in 4), approximately 25–35% is due to the Δ^1 isomer a (from the intensity of m/e 67 in 6) and the remaining 23–33% must be from the Δ^2 isomer b. Early in this work attempts were made to explain the loss of ethyl by ring contracting the methylcyclohexene to ethylcyclopentene followed by cleavage. The spectra of the deuterated compounds, and indeed that of ethylcyclopentene itself, clearly show that this is not the case.

That in fact additional fragmentation pathways than those shown in Scheme I are operating to a smaller extent is indicated by the lack of quantitative agreement with ion intensities predicted by this mechanism alone. Thus, when one attempts to explain the loss of methyl from ions h and i only, one is confronted with the problem of explaining the origin of the weak, but nevertheless real, peak at *m/e* 81, apparently due to loss of CD_3, in the spectrum of **5**. A possible formulation for this ion involves an alternate allylic cleavage in ion c.



The occurrence of alternate allylic cleavages is also necessary to explain the very large preponderance of the CH_3 loss (as opposed to the CH_2D and CHD_2 losses) in **6**. Thus the relatively few fragmentations shown in Scheme I only semiquantitatively explain the observed intensities of the mass shifted ions.

B. Methylenecyclohexanes.—The fragmentation pattern of the C_7H_{12} isomer methylenecyclohexane (**7**), shown in Figure 2, is quite similar to that of **3**. Since methylcyclohexene is the more stable isomer, *exo* → *endo* olefin isomerization might be expected to occur on electron impact. From the spectrum of **8**, it is apparent that loss of internal methyl is a bit more important in this series (47–52%, depending on the carbon source of *m/e* 82, *vs.* 40% in the methylcyclohexenes). From the spectrum of **8** one estimates that endocyclic isomerization prior to fragmentation is at least 80% complete since the spectrum exhibits an M − 17 peak which accounts for at least 48% of the total methyl loss. An assumption made here is that the fragmentation of the methylcyclohexene species obtained on isomerization is the same as that discussed above for **3**.

Hydrogen primarily from C-2 or C-6 is transferred to the exocyclic carbon atom during isomerization as shown by the large M − CH_2D ion at *m/e* 84 in the spectrum of **9**. Djerassi[9] has pointed out that a similar process occurs in 3,3,5,5-d_4 1 to produce a large M − 44 ion.

More extensive rearrangement of hydrogen atoms occurs in **7** than in **3**, even in the higher mass fragments. The ions at *m/e* 82 (M − CD_3) in the spectrum of **9**, at *m/e* 82 (M − CH_2D) in that of **8**, and very complex mass shift patterns in the loss of ethylene and ethyl fragments of **8** and **9** attest to this more complex fragmentation. This is not unexpected since one more allylic isomerization must occur before these fragmentations.

As mentioned previously the isomerization of an endocyclic olefin to the exocyclic position is apparently not important since there was no appreciable loss of a partially deuterated methyl group in the spectrum of **4**. There is no evidence for extensive randomization of hydrogen in the higher mass ions of **3** or its derivatives (although the weak *m/e* 69 ion in **4** can only be explained by multiple hydrogen transfers) but the ions of lower mass must have significant equilibration of hydrogen prior to formation (see the lower mass ions in Table I). For this reason no straightforward explanation of the origin of these ions can be postulated, in spite of the many deuterated derivatives which were studied.

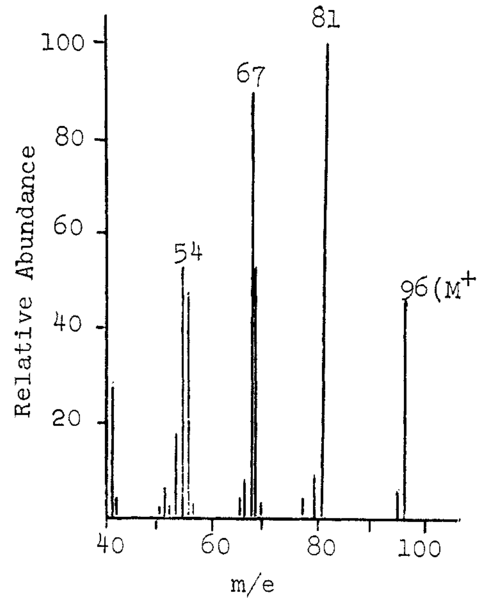


Figure 2.—Mass spectrum of methylenecyclohexane.

Conclusions

Allylic isomerization prior to fragmentation in the molecule radical ions of simple cyclic olefins certainly occurs, but this isomerization is slower than in acyclic olefins since hydrogen scrambling is not important in at least the higher mass fragment ions of the compounds reported here. Relatively more hydrogen randomization occurs in methylenecyclohexane than in methylcyclohexene due to the operation of a greater number of fragmentation mechanisms. An exocyclic double bond is more rapidly isomerized to an endocyclic position than *vice versa*. This study points out again[9] that mass spectrometric data must be carefully interpreted before it can be safely used in the structure elucidation of simple olefinic terpenes. Indeed, in the absence of extensive deuterium labeling, caution must be exercised in interpreting the spectrum of any olefin.

Experimental Section

General.—All compounds for which mass spectra were obtained were purified by collection from an Aerograph 200 gas chromatograph using 20% SE-30 as liquid phase dispersed on Chromosorb P. The infrared and nuclear magnetic resonance spectra of each compound were obtained using Perkin-Elmer 21 and Varian AR-60 instruments and were in complete accord with the assigned structures. All mass spectra were obtained using an Atlas CH_4 mass spectrometer operated at electron energies of 70 ev and lower, with the inlet and source temperatures maintained at approximately 110 and 160°, respectively.

7,7,7-d_3-Methylcyclohexene was prepared (34% yield after purification) by reaction of the Grignard reagent of trideuteriomethyl iodide[13] with cyclohexanone. The resultant alcohol was dehydrated by heating a concentrated ether solution of it with a few crystals of iodine and distilling the olefin directly from this mixture. The product after collection from a gas chromatograph had the isotopic composition 90.5% d_3, 8.5 d_2, and 0.5% d_1 as determined by mass spectroscopy.

2,2,6,6-d_4-Cyclohexanone was prepared by two equilibrations of 10 g of cyclohexanone, 20 ml of deuterium oxide, and 1.8 g of potassium carbonate at reflux temperatures for 4 days each. After careful distillation the product had the isotopic composition

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[13] R. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

of 88.9% d_4, 9.6% d_3, and 0.8% d_2 as determined by mass spectrometry.

2,6,6-d_3-Methylcyclohexene was prepared by the methyl Grignard dehydration sequence described above except an excess of Grignard reagent was used. The product, obtained in 37% yield, had isotopic composition 89% d_3, 10% d_2, and 1% d_0 after collection from a gas chromatographic column.

4,4-d_2-Methylcyclohexene.—Methylcyclohexen-4-one was prepared following the procedure of Braude and Webb.[14] Reduction of 2.86 g (0.026 mole) of methylcyclohexen-4-one with 0.25 g (0.007 mole) of lithium aluminum deuteride in 15 ml of anhydrous ether produced 2.5 g (83% yield) of crude methylcyclohexen-4-d_1-4-ol. The alcohol (0.022 mole) was dissolved in 20 ml of pyridine. The solution was cooled to 5° in an ice bath and 5 g (0.044 mole) of mesyl chloride dissolved in 10 ml of pyridine was added with stirring at such a rate that the solution remained below 10°. After storing the reaction mixture in a refrigerator overnight, water was added to it and two layers were separated. The aqueous layer was extracted with ether and the combined ether layers were washed many times with water. Crude mesylate (3.13 g, 74% yield) was obtained as an oil upon removal of the solvent.

The displacement of the mesylate was effected by treatment with 0.30 g (0.0072 mole) of lithium aluminum deuteride in 40 ml of anhydrous ether at 35° for 30 hr. The olefin, along with some ether, was removed from unreacted mesylate by distillation at low pressure and collected in a liquid nitrogen cooled trap. Final purification was effected by collection from a gas chromatographic column. The nuclear magnetic resonance spectrum indicated essentially quantitative deuteration. The mass spectrum indicated a deuterium incorporation of 96% d_2, 3% d_1, and 1% d_2. The contamination of the sample with a few per cent of monodeuteriomethylcyclohexadiene was obvious from this mass spectrum.

2,2,6,6-d_4-Methylenecyclohexane.—All glassware was oven dried. The dimethyl sulfoxide was dried over calcium hydride for 2 days and distilled into a flask containing type 4A molecular sieve.

Sodium hydride (1.4 g of a 55% dispersion in mineral oil, 0.0325 mole) was placed in a three-necked flask fitted with a condenser, nitrogen inlet, and dropping funnel. The flask was evacuated twice and filled each time with nitrogen. After the second flushing, nitrogen was passed continuously through the system. Dimethyl sulfoxide (12.5 ml) was added and the flask was heated to 75° and this temperature was maintained until the reaction was complete (approximately 50 min). The green-gray solution was cooled with an ice bath and 21.8 g (0.06 mole) of triphenylmethylphosphonium bromide dissolved in 50 ml of warm dimethyl sulfoxide was added with stirring. The reaction mixture became orange upon initial addition and dark yellow-green upon further addition. The reaction mixture was stirred for 15 min and 2.8 g (0.0285 mole) of 2,2,6,6-d_4-cyclohexanone (90% d_4) was added slowly, a slight exothermicity being noted. The solution was stirred for 40 min and all volatile compounds were immediately removed from the dimethyl sulfoxide at low pressures, 2.5 g (89% yield) of crude product being collected in a liquid nitrogen cooled trap. The pure olefin, after collection from a gas chromatograph, was shown by mass spectrometry to be 90% d_4.

7,7-d_2-Methylenecyclohexane was obtained in 30% over-all yield from pyrolysis at 505–510° of cyclohexane-d_2-carbinyl acetate, itself available by acetylation of the reduction product of methyl cyclohexanecarboxylate by lithium aluminum deuteride. A nuclear magnetic resonance spectrum of material purified by gas chromatography indicated quantitative deuteration. Its mass spectrum indicated greater than 98% d_2.

Registry No.—**3**, 591-49-1; **4**, 7721-69-9; **5**, 7721-70-2; **6**, 7721-71-3; **7**, 1192-37-6; **8**, 1560-57-2; 2,2,6,6-d_4-methylenecyclohexane, 3452-02-6; 2,2,6,6-d_4-cyclohexanone, 1006-03-7.

Acknowledgments.—This research was supported in part by grants from the Petroleum Research Fund (administered by the American Chemical Society) and the Research Corp.

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[14] A. Braude, A. A. Webb, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958).

Oxidation, Reduction, and Electrochemiluminescence of Donor-Substituted Polycyclic Aromatic Hydrocarbons[1]

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The effect of chemical structure on electrochemiluminescence (ECL) and the molecular properties associated with this phenomenon have been explored. Polarographic oxidation and reduction potentials and the fluorescence emission spectra in aprotic media of donor-substituted polycyclic aromatic molecules were measured. The stabilities of ion radicals generated from these compounds were determined by means of cyclic voltammetry. The results are in general agreement with the assumption that the efficiency of the ECL process is associated with the fluorescence, efficiency, and stability of the one-electron oxidation and reduction products under the experimental conditions. While multiple donor substituents on polycyclic aromatic nuclei result in fluorescent compounds with stable cations, the orientation of such substituents which is most effective in stabilizing the cation also results in extensive anion destabilization. The results are discussed in terms of molecular orbital theory.

The recent finding that successive chemical or electrochemical reduction and oxidation of fluorescent aromatic hydrocarbons in aprotic solvents where excess energy is available results in luminescent emission[2] (electrochemiluminescence or ECL) prompted our examination of other molecules which might exhibit this behavior. The usually fluorescent polycyclic aromatic hydrocarbons form stable anion radicals and unstable cation radicals in N,N-dimethylformamide (DMF). If it is assumed that anion–cation annihilation is an intermediate step in the ECL process, then cation stabilization should result in improved ECL efficiency. One way in which cation stabilization could be achieved is through multiple electron-donor substituents. While qualitative considerations suggest that such substituents would exert a deleterious effect on fluorescence efficiency and anion-radical stability, quantitative evaluations of such effects have not been made. The advantages of cation-radical stabilization could outweigh these destabilizing factors in the over-all ECL

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[1] Cumulative Influence of Substituents on the π-Electron Properties of Aromatic Systems. XI.

[2] *Cf.* A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Am. Chem. Soc.*, **88**, 2864 (1966), and references therein.