Acid-Catalyzed and Thermal Isomerization in the Methylcyclohexadiene System. Elimination of Ethanol from Ethyl Methylcyclohexenyl Ethers

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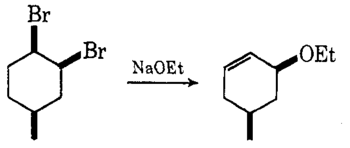
Received July 1, 1970

Acid-catalyzed elimination of ethanol from various ethyl methylcyclohexenyl ethers by either activated alumina at elevated temperatures or potassium hydrogen sulfate yields complex mixtures of all possible methyl-1,3-cyclohexadienes, 3-methylenecyclohexene, and toluene. At 250 and 300°, the products are consistent with simple eliminations involving intermediary allylic carbonium ions, followed by alumina-catalyzed isomerization of the diene mixture, although the mechanism by which this occurs is obscure. Thermal isomerization of the product methyl-1,3-cyclohexadienes *via* [1,5]-sigmatropic hydrogen migration is not important at temperatures much below 325° under nonequilibrium fast-flow conditions, although alumina-catalyzed isomerization is extensive.

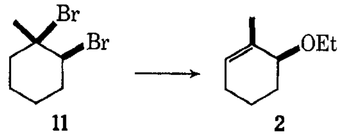
In our investigations of the various mechanistic pathways involved in the alumina-catalyzed vapor phase dehydration of substituted hexadienols,[2] we recently postulated that the complex product mixtures can be rationalized on the basis of electrocyclic ring closure of intermediate trienes followed by cyclohexadiene isomerization resulting from intramolecular [1,5]-sigmatropic hydrogen shifts. At that time, however, we had no direct experimental evidence for the latter portion of this mechanism, nor could we estimate the relative contribution of acid-catalyzed isomerization of the product methyl-1,3-cyclohexadienes. We would now like to report on the magnitude and relative contributions of both acid-catalyzed and thermal isomerization in the generation of the methyl-1,3-cyclohexadiene system.

Most preparations of alkyl-1,3-cyclohexadienes reported in the literature involve, as the final step, an acid-catalyzed elimination reaction. One procedure which can be utilized is that of Hofmann and Damm,[3] which generates the diene system by acid-catalyzed decomposition of an appropriately substituted cyclohexenyl ethyl ether. Pines and coworkers[4,5] reported the synthesis of several substituted 1,3-cyclohexadienes by this procedure. In some instances isomerization occurred,[5] but for the most part unrearranged cyclohexadienes were reported as primary products. Thus this system seemed to be well suited to determine the extent of acid-catalyzed isomerization of the cyclohexadiene products by comparison of the alumina and potassium hydrogen sulfate product ratios.

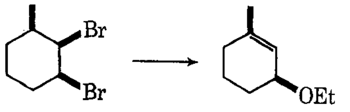
Bromination of the three isomeric methylcyclohexenes was accomplished in good yield. Reaction of the resulting purified bromides with sodium ethoxide yielded the desired methylcyclohexenyl ethyl ethers whose structures and purities were confirmed by nmr and glpc. The results are illustrated in eq 1–3.



10 **1** (1)



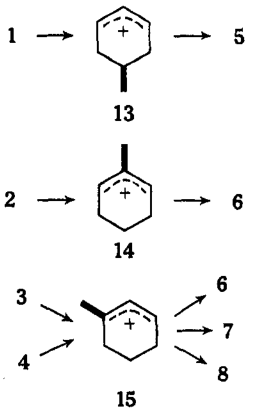
11 **2** (2)



12 **3** (3)

Methylcyclohexadienes were generated from ethyl methylcyclohexenyl ethers or methylcyclohexenols by either of the following: (1) distillation from potassium hydrogen sulfate, or (2) vapor phase passage over alumina (250–300°). Similarly, isomerization of methyl-1,3-cyclohexadiene mixtures of known composition was accomplished by passage through a dehydration column packed with either Pyrex helices or alumina (300–350°). Table I summarizes the results of the elimination reactions, while the thermolytic results are shown in Table II.

Distillation of either **1**, **2**, or **3** from potassium hydrogen sulfate or passage through an activated alumina column at 250–300° produced mixtures of the desired methyl-1,3-cyclohexadienes. In no case was a pure product obtained, although the major product in each was that predicted on the basis of simple 1,2 elimination. A much more reasonable supposition, however, is that each ether procedes through an allylic carbonium ion from which the dienic products are then formed. This would explain the product distribution obtained from alumina-catalyzed elimination to a first approximation.



Examination of the results obtained in Table I shows that **1** and **2** do yield the expected methyl-1,3-cyclohexadienes **5** and **6** in good yield at 250°. In confirmation of the intermediacy of **15**, both **3** and **4** were passed over alumina at 250°, and similar product distributions were obtained. The differences in minor product for-

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(1) Author to whom inquiries are to be addressed.

(2) C. W. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

(3) F. Hofmann and P. Damm, *Mitt Kohlenforschungsmit Breslau*, **2**, 113, 127 (1925); *Chem. Abstr.*, **22**, 1249 (1928).

(4) H. Pines and R. H. Koslowski, *J. Amer. Chem. Soc.*, **78**, 3776 (1956).

(5) H. Pines and C. Chen, *ibid.*, **81**, 928 (1959).

TABLE I
ACID-CATALYZED ELIMINATION PRODUCTS

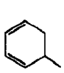
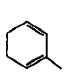
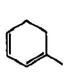
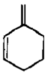
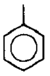
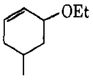
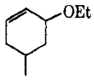
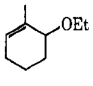
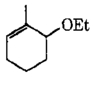
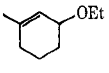
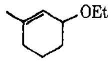
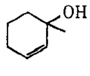
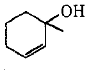
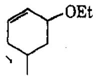
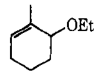
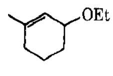
Compd (no.)		Catalyst (temp, °C)	% of total product				
			 5	 6	 7	 8	 9
	(1)	Al_2O_3 (250)	73	6	10	4	7
	(1)	Al_2O_3 (300)	73	7	11	3	5
	(2)	Al_2O_3 (250)	8	69	8	9	6
	(2)	Al_2O_3 (300)	7	29	41	14	9
	(3)	Al_2O_3 (250)	12	24	41	14	9
	(3)	Al_2O_3 (300)	13	24	39	15	9
	(4)	Al_2O_3 (250)	0	39	27	34	0
	(4)	Al_2O_3 (300)	1	33	46	20	0
	(1)	$KHSO_4$ (100)	73	8	14	4	1
	(2)	$KHSO_4$ (100)	0	41	35	22	2
	(3)	$KHSO_4$ (100)	18	18	46	14	2

TABLE II
THERMOLYSES OF METHYL-1,3-CYCLOHEXADIENES[a]

Support (temp, °C)	Feed mixture, % of total			Product mixture, % of total		
	1-Me	2-Me	5-Me	1-Me	2-Me	5-Me
Helices (300)	12	8	80	13	8	79
Al_2O_3 (300)[b]	12	8	80	35	25	26
Helices (325)	12	8	80	41	12	47
Al_2O_3 (325)[c]	12	8	80	41	27	15
Helices (350)	15	8	77	61	25	13
Al_2O_3 (350)[d]	15	8	77	42	28	11
Helices (350)	46	54	0	51	41	8
Helices (350)	56	22	22	57	29	14

[a] Sealed tube, 150°, 24 hr or until no further change: 70% 1-Me, 20% 2-Me, 10% 5-Me. [b] 7% **8** and 7% **9** also formed. [c] 9% **8** and 7% **9** also formed. [d] 9% **8** and 10% **9** also formed.

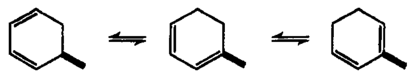
mation (**5** and **9**) can be attributed to kinetic control in the major product formation step, followed by separate isomerization reactions leading to **5** and **9**.

Elimination of ethanol from **1**, **2**, and **3** by the action of potassium hydrogen sulfate yields results similar to those obtained from alumina, indicating extensive isomerization of the initial product or rearrangement of the intermediate carbonium ions. One major difference between the alumina and $KHSO_4$ reactions is the percentage of toluene. The methylcyclohexadiene to toluene conversion over alumina is well known[6] and can be a serious side reaction; hence this variance in products is to be expected.

In order to estimate the magnitude of acid-catalyzed isomerization of methyl-1,3-cyclohexadienes formed by the elimination of ethanol or water, a mixture of known composition was thermolyzed at 300, 325, and 350° over both alumina and Pyrex helices. It can readily be seen that at 300 and 325° the quantity of thermal isomerization is much less than the corresponding passage over alumina. While the absolute numbers are obviously dependent on type of alumina, flow rate,[7] porosity, etc., it does indicate that the more important mode of cyclohexadiene isomerization at temperatures much below 350° is alumina-catalyzed as opposed to [1,5]-sigmatropic hydrogen migration which is dominant at temperatures of 350° or higher.

These results substantiate, to a large degree, our previous postulate that substituted 1,3-cyclohexadienes undergo rapid reversible isomerization resulting in a dynamic mixture of positional isomers in any reaction in which these structures are generated at elevated temperatures. However, we tended to ascribe this isomerization almost exclusively to rapid reversible thermal [1,5]-sigmatropic rearrangement of hydrogen. As can readily be seen from the thermal studies, this is a facile process at 350°, and possible at 325°, but becomes much less important at 300 and 250°. That the process is a dynamic set of equilibria is apparent from examination of initial *vs.* final product ratios. Isomerization occurs in the direction one would predict for the expected thermodynamic distributions,[8] although it would be entirely fortuitous and quite unexpected if these values actually correspond to equilibrium values at 350°. It must be kept in mind that all of these experiments attempt to duplicate on-column nonequilibrium flow conditions followed by rapid quenching. It would therefore be unrealistic to expect equilibrium to be achieved during the relatively short residence times[9] in the hot zones.

The appearance of the less stable 5-methyl-1,3-cyclohexadiene in all cases regardless of its presence or absence in the feed mixture indicates the reversibility of the [1,5] shifts under thermolytic conditions. The possibility of carbonium mechanisms operating at these temperatures (325° and above) was eliminated by adding 3-methylenecyclohexene to any of the above mixtures. In all cases, the exocyclic diene survives quantitatively. This, we feel, further substantiates the sigmatropic nature of the isomerization in the absence of alumina in that this diene cannot assume the necessary cisoid configuration.[10] Further, Bates and coworkers[8] have defi-



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[6] C. W. Spangler, *J. Org. Chem.*, **31**, 346 (1966).

[7] It is of particular importance in comparing results between alumina and helices that the flow rates be matched quite accurately and maintained throughout the course of the reaction.

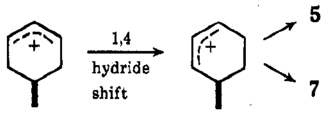
[8] R. B. Bates, E. S. Caldwell, and H. P. Klein, *ibid.*, **34**, 2615 (1969).

[9] It has been estimated here and previously (see ref 1) that contact or residence times in the heated zone is *ca.* 45 sec.

[10] (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie–Academic Press, Weinheim/Bergstr., 1970, pp 114–140.

nitely shown that exocyclic and endocyclic dienes will equilibrate under either acid or base catalysis.

The question remains, once one eliminates sigmatropic hydrogen migration as a specific cause, as to the probable source of cyclohexadiene isomerization at temperatures below 300°. Alumina, presumably *via* acid catalysis, is capable of causing such isomerization and in so doing also generates **8** and **9**. A comparison of product distributions (Table II) at 250 and 300° shows an apparent anomally for **1** in that the product ratios appear to be independent of temperature. In fact, $KHSO_4$ elimination produces an almost identical distribution for **1** at a temperature at least 100° lower. A somewhat similar observance may be made for **3**, while for **2** there is a large temperature dependence and nonsimilar results with $KHSO_4$. These observations of product distributions indicate that kinetic control of product formation is operative. If such is the case, an alternative explanation to acid-catalyzed isomerization would be rearrangement of the intermediate allylic carbonium ions **13**, **14**, and **15**, probably *via* hydride shifts, for example



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It is indeed possible, if not probable, that rearrangements involving 1,2-, 1,3-, and 1,4-hydride shifts compete with acid catalysis throughout the whole range of temperatures normally utilized in cyclohexadiene production, and that the observed product distributions at various temperatures are the sum of several independent kinetically controlled isomerization pathways. Therefore, even though we have shown that alumina can cause isomerization, the exact mechanism, if indeed only one exists, remains obscure. Sigmatropic isomerization, however, does not assume major proportions until reactions approach 325° in a nonequilibrium flow situation.

Experimental Section[11]

3-Ethoxy-5-methylcyclohexene (**1**).—1,2-Dibromo-4-methylcyclohexane[12] (384 g, 1.5 mol) was added to a mixture of sodium (4 g-atoms) in 1200 ml of absolute alcohol. The mixture was refluxed for 4 hr, cooled, and filtered to remove precipitated sodium bromide. The salt was washed with several 200–300-ml portions of ether, and the combined organic solution was washed with several 200-ml portions of water. The resulting ether solution of **1** was then separated and dried with anhydrous magnesium sulfate. Distillation at reduced pressure yielded **1** (130 g, 62%), bp 60–62° (14 mm), $n^{27}\text{D}$ 1.4464 (lit.[13] bp 155°, $n^{18}\text{D}$ 1.4490). Glpc indicated a purity of at least 96%, with a trace of the isomeric 3-ethoxy-6-methylcyclohexene. The nmr spectrum revealed a multiplet, τ 4.3 (2 vinyl protons); multiplet, τ 5.9–6.7 (3 protons α to ether linkage); broad multiplet, 7.8–8.6 (5 protons, methylene and methyne); triplet, τ 8.8 (3 protons, ether methyl, J = 6 Hz); multiplet, τ 9.1 (3 protons, alicyclic methyl).

3-Ethoxy-2-methylcyclohexene (**2**).—1,2-Dibromo-1-methylcyclohexane[14] (243 g, 0.95 mol) was treated as described above for **1**. Distillation at reduced pressure yielded **2** (67 g, 51%), bp 54–56° (14 mm), $n^{25}\text{D}$ 1.4535 [lit.[15] bp 61–62° (15 mm), $n^{21}\text{D}$ 1.4550]. Glpc indicated a purity of at least 97%, with a trace of the isomeric 3-ethoxy-3-methylcyclohexene. The nmr spectrum revealed a broad singlet, τ 4.4 (1 vinyl proton); multiplet, τ 6.1–6.8 (3 protons α to ether linkage); broad multiplet, 8.3 (9 allylic and methylene protons); triplet, τ 8.8 (3 protons, ether methyl, J = 7 Hz).

3-Ethoxy-1-methylcyclohexene (**3**).—1,2-Dibromo-3-methylcyclohexane[16] (266 g, 1.04 mol) was treated as described above for **1** and **2**. Distillation at reduced pressure yielded **3** (56 g, 43%), bp 58–60° (11 mm), $n^{25}\text{D}$ 1.4533. Glpc indicated a purity of at least 95% with a trace of 3-ethoxy-4-methylcyclohexene. The nmr spectrum revealed a multiplet, τ 4.2–4.6 (1 vinyl proton); multiplet, τ 6.1–6.8 (3 protons α to ether linkage); multiplet, τ 7.9–8.6 (9 allylic and methylene protons); triplet, τ 8.8 (3 protons, ether methyl, J = 7 Hz).

Alumina-Catalyzed Eliminations. A.—Through a 22-mm Pyrex tube packed to a depth of 12 in. with activated alumina[17] (8–14 mesh) and externally heated at 250° with a Lindberg Hevi-duty split-tube electric furnace was dropped 3-ethoxy-5-methylcyclohexene (20 g, 0.16 mol) at the rate of 0.5 ml/min. The alumina had been dried previously by heating the column at 300° under vacuum for 1 hr. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice–acetone bath and subsequently warmed to room temperature, washed with water, and dried by filtration through anhydrous magnesium sulfate. After filtration the clear yellow liquid was distilled at reduced pressure and the volatile fraction collected. No attempt was made to maximize the yield (14 g, 93%). Glpc analysis showed the presence of five products. Each peak emanating from the chromatograph was trapped in a V tube immersed in a Dry Ice bath and identified by characteristic and known uv and nmr spectra:[2] 73% **5**, 6% **6**, 10% **7**, 4% **8**, and 7% **9**.

B.—3-Ethoxy-5-methylcyclohexene (20 g, 0.16 mol) was allowed to react as above at 300°. The crude product was isolated and purified (85% yield). Glpc analysis revealed the presence of the same five products: 73% **5**, 7% **6**, 11% **7**, 3% **8**, and 5% **9**.

C.—3-Ethoxy-2-methylcyclohexene (15 g, 0.12 mol) was allowed to react as above at 250°. Glpc analysis of the purified product (80%) yielded 8% **5**, 69% **6**, 8% **7**, 9% **8**, and 6% **9**.

D.—3-Ethoxy-2-methylcyclohexene (20 g, 0.16 mol) was allowed to react as above at 300°. Glpc analysis of the purified product (83%) yielded 7% **5**, 29% **6**, 41% **7**, 14% **8**, and 9% **9**.

E.—3-Ethoxy-1-methylcyclohexene (20 g, 0.16 mol) was allowed to react as above at 250°. Glpc analysis of the purified product (92%) yielded 12% **5**, 24% **6**, 41% **7**, 14% **8**, and 9% **9**.

F.—3-Ethoxy-1-methylcyclohexene (20 g, 0.16 mol) was allowed to react as above at 300°. Glpc analysis of the purified product (90%) yielded 13% **5**, 24% **6**, 39% **7**, 15% **8**, and 9% **9**.

G.—1-Methyl-2-cyclohexen-1-ol (20 g, 0.18 mol) was allowed to react as above at 250°. The crude product was filtered directly through anhydrous magnesium sulfate and distilled (12.9 g, 76%). Glpc analysis of the product yielded 39% **6**, 27% **7**, and 34% **8**.

H.—1-Methyl-2-cyclohexen-1-ol (20 g, 0.18 mol) was allowed to react at 300° and isolated as in G (13.2 g, 78%). Glpc analysis of the product yielded 1% **5**, 33% **6**, 46% **7**, and 20% **8**.

$KHSO_4$-Catalyzed Eliminations. A.—3-Ethoxy-5-methylcyclohexene (0.18 mol) was distilled from potassium hydrogen sulfate (0.036 mol). The distillate was collected in an ice-cooled flask and washed with dilute bicarbonate solution and the organic product was dried with anhydrous magnesium sulfate. The product (7.0 g, 41%) was distilled, bp 98–108°. Glpc analysis revealed 73% **5**, 8% **6**, 14% **7**, 4% **8**, and 1% **9**.

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[11] Gas–liquid partition chromatography was performed with an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370 electronic integrator for peak area measurement; dual 6'-15% Carbowax 20M on 60–80 mesh Chromosorb W columns were utilized for the determination of ether purity, dual 15'-15% TCEP on 60–80 mesh Chromosorb W columns for the analysis of the methycyclohexadiene product mixtures. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202, nmr spectra with a Varian A60-A using TMS as an internal standard ($CDCl_3$ solvent). All spectra were consistent with the assigned structures, and satisfactory C and H analyses were obtained for all compounds.

[12] M. Mousseron and R. Granger, *C. R. Acad. Sci.*, **205**, 327 (1937).

[13] M. Mousseron and F. Winternitz, *Bull. Soc. Chim. Fr.*, **13**, 232 (1946).

[14] M. Mousseron and F. Winternitz, *ibid.*, **13**, 604 (1946).

[15] E. Urion, *C. R. Acad. Sci.*, **199**, 363 (1934).

[16] A. Berlande, *Bull. Soc. Chim. Fr.*, **9**, 644 (1942).

[17] Kaiser active alumina KA-101 (Matheson Scientific); chemical analysis and physical properties available for supplier upon request.

B.—3-Ethoxy-2-methylcyclohexene (0.18 mol) was treated as described above, yielding 6.6 g (38%) of mixed dienes. Glpc analysis yielded 41% **6**, 35% **7**, 22% **8**, and 2% **9**.

C.—3-Ethoxy-1-methylcyclohexene (0.18 mol) was treated as above yielding 7.0 g (41%) of mixed dienes. Glpc analysis yielded 18% **5**, 18% **6**, 46% **7**, 14% **8**, and 2% **9**.

Thermal Isomerization Reactions. General Procedure.—Mixtures of the three isomeric methyl-1,3-cyclohexadienes of known composition were added dropwise through a 22-mm Pyrex tube packed to a depth of 12 in. with $^1/_{16}$-in. Pyrex helices and externally heated at either 300, 325, or 350° as in the above elimination studies. The thermolysis products were isolated in a similar manner (90–95% recovery) and submitted to glpc analys is (Table II). Addition of 3-methylenecyclohexene did not affect the above reactions, and **8** survived quantitatively in all cases. Alumina studies were carried out under identical conditions of temperature and flow rate.

Registry No.—**1**, 27525-90-2; **2**, 27525-91-3; **3**, 27525-92-4; **4**, 23758-27-2; ethanol, 64-17-5.

The Molecular Structure of Perfluorobutyne-2 and Perfluorobutadiene-1,3 as Studied by Gas Phase Electron Diffraction

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Received July 6, 1970

The structures of two C_4F_6 isomers, perfluorobutadiene-1,3 and perfluorobutyne-2, have been determined by gas phase electron diffraction. The perfluorobutyne-2 was found to be linear with freely rotating CF_3 groups. The following parameters were determined: r_g values for ($C\equiv C$) = 1.199 ± 0.009 Å; (C–F) = 1.333 ± 0.003 Å; (C–C) = 1.472 ± 0.006 Å; and $\angle$CCF = 110.8 ± 0.3°. In contrast to the trans planar structure of butadiene-1,3, the perfluoro compound is in a nonplanar cisoid conformation, with a CCCC dihedral angle of 47.4 ± 2.4°. For the other structural parameters (r_g values): (C=C) = 1.336 ± 0.018 Å; (C–F) = 1.323 ± 0.006 Å; (C–C) = 1.488 ± 0.018 Å; $\angle C{=}C{-}C$ = 125.8 ± 0.6°; $\angle F_7{-}C_2{=}C_1$ = 121.0 ± 1.8°; and $\angle F_6{-}C_1{=}C_2$ = 124.5 ± 0.6°. The above uncertainties were estimated errors set at three times the standard deviations as obtained from the converged least squares fitting of the calculated to the observed $qM(q)$ function.

Recent developments in experimental techniques, both diffraction and spectroscopic, and in computer reductions of data have led to accurate determinations of molecular structures and systematic studies of geometrical parameters as influenced by various types of substitution. It was recognized more than a decade ago[1,2] that C–C bond lengths vary with environment. Stoicheff[3] found empirical relations for C–C and C=C bond lengths in hydrocarbons as a function of the number of adjacent bonds or adjacent atoms. Little is known about the secondary effect,[4] of deviations due to adjacent heteroatoms, although Stoicheff[3] did notice a small change on the C=C bond length when Cl, Br, or F atoms were substituted for hydrogen. There is a suggestion of an "inductive" effect through two or more bonds by heteroatoms, but it has not been adequately documented. Of course, Stoicheff's relations do not apply to highly strained small ring molecules.[5,6]

Studies of fluoro compounds made in this laboratory have shown that substitution not only changes the length of the bond β to the site of substitution, but also alters the entire molecular conformation. For instance, perfluoroazomethane[7] was found to be cis instead of trans, as is the conformation for azomethane, and the third carbon atom of perfluoropropene may not be in the plane containing the $F_2C{=}C$ group.[8] This is a report on the molecular structures of two fluorocarbons, $F_3CC\equiv CCF_3$ and $F_2C{=}CFCF{=}CF_2$, which were investigated in order to shed additional light on the inductive effect produced by fluorine atom substitution.

Perfluorobutyne-2 was first studied by Sheehan and Schomaker,[9] who used visual estimates of plate densities. They reported (C–F) as 1.340 ± 0.020 Å, (C–C) as 1.465 ± 0.055 Å, ($C\equiv C$) as 1.22 ± 0.09 Å, and $\angle$FCF as 107.5 ± 1.0°, in agreement with corresponding geometrical parameters in $F_3CC\equiv CH$.[9] Infrared and raman spectra of $F_3CC\equiv CCF_3$ were obtained by Miller and Bauman.[10] Their data clearly indicate that D_{3d} selection rules were followed. Hence either the molecule has free internal rotation or a staggered conformation; they were unable to distinguish between them.

The structure of butadiene-1,3 with various degrees and types of substitution has been extensively investigated. In general, these were found to be in the trans-planar conformation.[11–14] However, in the cases with trihalogenation at the 1,1, and 3 positions, skew conformations were observed.[15] For the hexasubstituted species, there is strong evidence for a cisoid structure.[16,17] Robin and Brundle recorded the optical spectra of perfluorobutadiene-1,3 and interpreted their data as indicative of a cisoid structure, with the skeleton carbon dihedral angle of approximately 42°.[18] In view of this departure from the expected behavior of a conjugated system, it was

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