The filtrate was flash evaporated to yield 8.22 g. (96.0%) of a yellow-orange solid, which was recrystallized from petroleum ether (b.p. 30–60°) to yield 8.15 g. of XVIII, m.p. 39–40° (lit.[41] m.p. 39–40°). This product also was a strong vesicant and lachrymator. Its infrared spectrum in Nujol exhibited absorption bands at 2410 (—SCN), 1672 (C═O), and 1550 (C═C) cm.$^{-1}$. The ultraviolet spectrum in 95% ethanol exhibited maximal absorption at 205 mμ (ε 1154) and 276.5 (9234).

Preparation of 1-(N,N-Dimethylamino)-1-buten-3-one (XIX).—In a 250-ml. erlenmeyer flask was placed 70 ml. (0.621 mole) of a 40% aqueous solution of dimethylamine. To this solution was added dropwise, with stirring and ice cooling, 16 g. (0.15 mole) of I. After 0.5 hr. at room temperature the mixture was saturated with solid potassium carbonate and continuously extracted with ether for 12 hr.; the ether extracts were dried over anhydrous magnesium sulfate and distilled to yield 8.17 g. (72%) of XIX, b.p. 132–133° (20 mm.), n^{20}_{D} 1.5560 [lit.[42] b.p. 131–133° (20 mm.), n^{20}_{D} 1.5562]. The infrared spectrum exhibited a strong carbonyl band at 1664 cm.$^{-1}$. A band at 960 cm.$^{-1}$ indicated a *trans* arrangement with the double bond. The ultraviolet spectrum 95% ethanol exhibited maximal absorption at 302 mμ (ε 24,900).

Preparation of Methyl β-Cyanovinyl Ketone (XX).—In a 250-ml. erlenmeyer flask was placed 16.37 g. (0.10 mole) of X, 150 ml. of benzene, and 6.51 g. (0.10 mole) of potassium cyanide. To this solution was added 5.0 g. (0.052 mole) of trimethylamine hydrochloride in 5 ml. of water. The reaction mixture was heated to 50°, whereupon a solution of 3.25 g. (0.05 mole) of potassium cyanide in 15.0 ml. of water was added dropwise with stirring. Evolution of trimethylamine was observed. On cessation of trimethylamine evolution, the benzene layer was decanted and a new portion of benzene (100 ml.) added. The mixture was heated at 50° for 1 hr. with stirring, whereupon the benzene layer was decanted and a fresh portion of benzene added. The entire process was repeated twice more. The benzene extracts were combined, dried over anhydrous sodium sulfate, and distilled to yield 5.21 g. (54.9%) of XX, b.p. 71° (11 mm.), n^{20}_{D} 1.4622 [lit.[40] b.p. 73° (11 mm.), n^{27}_{D} 1.4590]. The infrared spectrum (neat) exhibited absorption bands at 2232 (C≡N), 1706 (C═O), and 1618 cm.$^{-1}$ (C═C). A strong band at 965 cm.$^{-1}$ indicated a *trans* arrangement about the double bond. The ultraviolet spectrum exhibited maximal absorption at 226 mμ (ε 8384).

Acknowledgment.—The authors wish to thank Dr. M. Hanna and Dr. C. DePuy for their kind advice

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[42] N. K. Kochetkov, *Izvest. Akad. Nauk. SSSR Otdel. Khim. Nauk*, 991 (1953); *Chem. Abstr.*, **49**, 2308 (1955).

The Autoxidation of 4-Vinylcyclohexene[1a]

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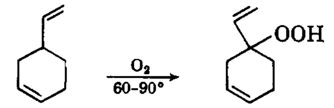
4-Vinylcyclohexene has been found to be autoxidized predominantly at the secondary allylic positions. All of the possible allylic hydroperoxides are formed to some extent. A similar product distribution is obtained from the attack on the olefin of *t*-butoxy radicals generated from *t*-butyl hydroperoxide–cobalt naphthenate and *t*-butyl peroxybenzoate–cuprous bromide.

The Diels–Alder dimer of butadiene, 4-vinylcyclohexene (**1**), has been reported[2] to be autoxidized in the liquid phase to yield the tertiary hydroperoxide **3b** exclusively. This result requires that the propagative species in the autoxidation chain, presumably a peroxy radical, removes a tertiary allylic hydrogen to the exclusion of the more abundant secondary. By contrast, our preliminary experiments with this system indicated that the oxidation produced a mixture of predominantly secondary hydroperoxides. Thus, the hydroperoxides could be catalytically hydrogenated and the resulting alcohols oxidized to a mixture of ketones in which the most abundant component would be 3-ethylcyclohexanone. A quantitative determination of the hydroperoxides produced in this autoxidation could provide valuable information regarding the selectivity of peroxy radicals toward attack on allylic carbon–hydrogen bonds of several types. Hence, our efforts were directed toward examining the isomer distribution obtained under differing conditions of temperature, solvent and initiation.



1 **3b**

The autoxidation of **1** was effected by passing oxygen through the pure olefin or concentrated solutions of the olefin in *n*-decane, benzene, or *t*-butylbenzene at 60–80°. Most of the runs were terminated after sufficient oxygen was absorbed to oxidize 10–12% of **1**, but some cases were examined at conversion levels of 6 and 23%. Conversion level appeared to have no effect on isomer distribution. In a few instances, azobisisobutyronitrile (AIBN) initiation was employed. At low concentrations, AIBN had little effect, but at higher concentrations it eliminated a short induction period and increased the rate of oxygen absorption.

For low conversion runs, hydroperoxide of acceptable purity could be obtained by evaporation of the unoxidized olefin and evaporative distillation of the residue. The runs at higher conversions required extraction of the hydroperoxide with cold, dilute base and distillation to obtain hydroperoxide of satisfactory purity. Hydroperoxide with *ca.* 86% of the theoretical active oxygen could be obtained. It was feared that selective loss of secondary hydroperoxide by base-catalyzed decomposition[3] might occur during the extraction step, but a comparison of runs worked up by the two methods showed that these losses, if any, were not serious. That the distillation step (and the subsequent manipulations involved in analysis) did not change the isomer distribution was shown by analysis of the crude hydroperoxide by n.m.r. The secondary hydroperoxide fraction was estimated from a comparison of the area for the >CH-OO– hydrogen

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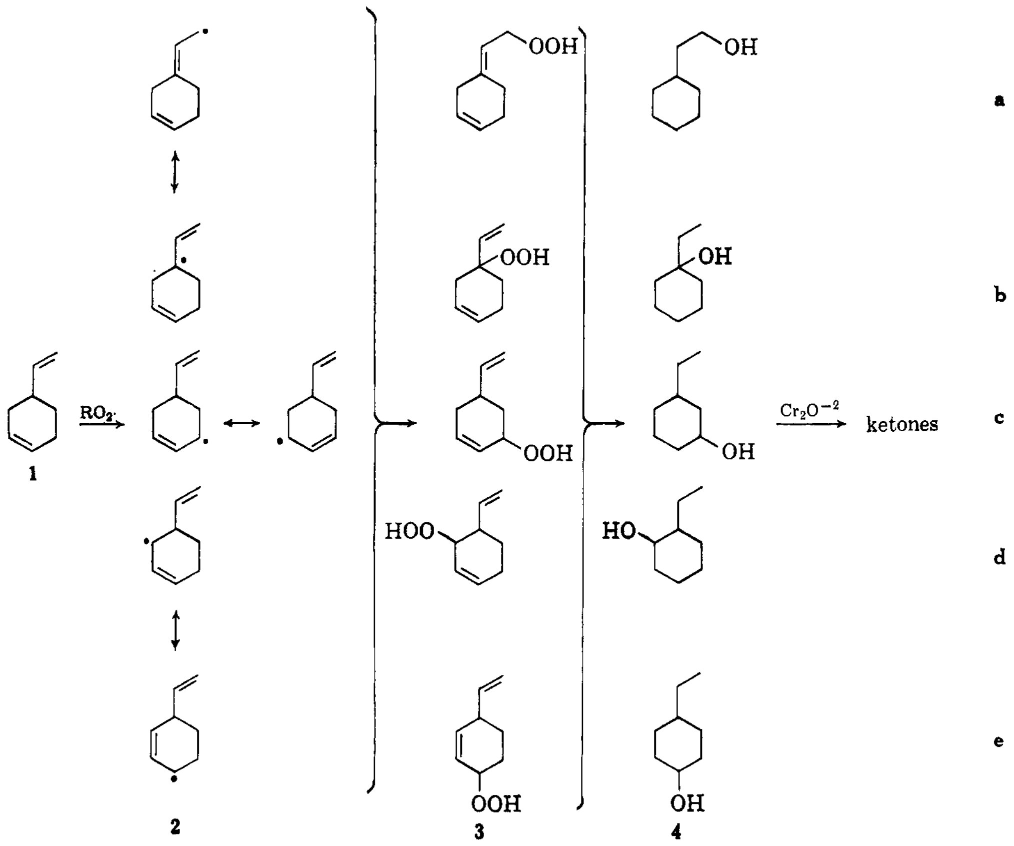
[1] (a) Presented at the 18th Southwest Regional Meeting, American Chemical Society, Dallas, Tex., December 6, 1962; (b) The Carwin Company, Stiles Lane, North Haven, Conn.

[2] W. F. Brill, *J. Org. Chem.*, **24**, 257 (1959).

[3] N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, **73**, 880 (1951).

CHART I



with the area for the –OO–H hydrogen. Subsequent analysis by the scheme outlined below indicated 86.5% secondary, as compared with the 87% estimate by n.m.r.

The yield of hydroperoxide isolated by either of these procedures was only 55–65% based on oxygen uptake. No significant loss of active oxygen was apparent on heating a solution of the hydroperoxide in **1** under the reaction conditions; the active oxygen content dropped from 1.34% to 1.24% in 3 hr. at 80°. Some of the input oxygen is involved in formation of the polymeric peroxide which is always observed. In addition, the nonperoxidic fraction of the oxidation mixture contains alcohols and ketones derived from **1**. This portion of the oxidate was analyzed in the same manner as the hydroperoxide and shown to contain approximately the same isomer distribution. The hydroperoxide and ketone–alcohol fractions account for 90% of the input oxygen.

In order to determine the isomer distribution, the hydroperoxide mixture was hydrogenated to a mixture of ethylcyclohexanols, and the alcohols were oxidized to the corresponding ketones. Both alcohol and ketone mixtures were analyzed with gas–liquid partition chromatography (g.l.p.c.) by comparing retention times and peak areas with those for known mixtures of the expected components. In addition to the identification based on g.l.p.c. retention times, the major ketone component was isolated on a preparative-scale g.l.p.c. column and shown to be 3-ethylcyclohexanone by comparison of its semicarbazone with an authentic sample. The infrared spectrum of a known ketone mixture made up according to the g.l.p.c. analysis of an unknown, corresponded closely to the infrared spectrum of the unknown.

From peroxy radical attacks on **1** at the available allylic carbons, five hydroperoxide products might be anticipated as shown in Chart I. Hydrogenation produces a mixture of eight alcohols (including the *cis–trans* isomers of **4c**, **d**, and **e**) in which **4a** and **b** were determined by g.l.p.c. analysis on a packed column. The weight % of each component was obtained directly from calibration data. It was not possible to resolve completely the *cis–trans* pairs of the remaining secondary alcohols; so these were determined as the ketones. The only g.l.p.c. column available which achieved the necessary separation of all three ketone isomers was a 300-ft. capillary column coated with Carbowax 20M. A great deal of difficulty was experienced in obtaining reproducible areas for individual peaks, presumably due to variations in sample size. It was found that good reproducibility could be obtained for ratios of peak areas, and the ketones were analyzed on this basis. Results, normalized to 100%, are shown in Table I.

It is apparent from these data that the secondary allylic hydrogens are attacked preferentially and that the isomer distribution does not vary significantly over the limited ranges of temperature and diluents studied. Comparison of these results, in which peroxy radicals are the hydrogen-abstracting species, with those reported by Shelton and Henderson[4] for reaction of **1** with *t*-butyl hydroperoxide–cobalt naphthenate reveals an obvious discrepancy. For their system, in which *t*-butoxy radicals are the presumed hydrogen abstractors, a predominant secondary attack occurs also, but their analysis failed to reveal a product derivable from radical **2e** (Table II). In the interest of securing further information regarding the attack

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[4] J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, **26**, 2185 (1961).

Table I

Isomer Distribution in Autoxidation of 4-Vinylcyclohexene

Diluent	AIBN init., g.,	Temp., °C.	% **4a**	% **4b**	% **4c**	% **4d**	% **4e**
None		60	*b*	11.8 ± 0.7[a]	59.4 ± 2.6	11.9 ± 2.7	16.9 ± 0.7
None	0.1[c]	60	3.5	11.9	*b*	*b*	*b*
None	1.0[c]	60	2.0	10.6	*b*	*b*	*b*
None		75	*b*	10.2 ± 1.3	65.1 ± 1.6	8.3 ± 0.4	16.4 ± 0.1
t-BuC_6H_5[d]		75	3.3	10.0	63.4	7.9	15.4
C_6H_6[d]		82	*b*	9.0	65.1	7.2	18.7
n-Decane[d]		82	*b*	11.7	65.1	7.8	15.5

[a] Average deviation from the mean of duplicate runs. [b] Mixture not analyzed for this component. [c] For 100 ml. of olefin. [d] Fifty volume %.

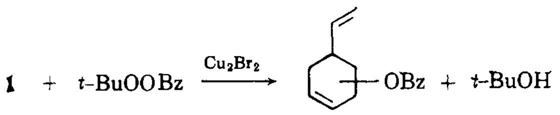
Table II

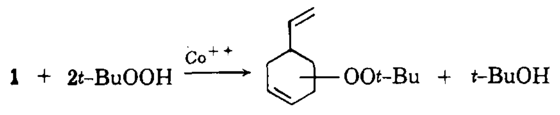
Position of *t*-Butoxy Radical Attack on 4-Vinylcyclohexene

Radical source, temp., °C.	% **4b**	% **4c**	% **4d**	% **4e**
t-BuOOH-Co^{+2}, 45–55[a]	1–3	75–85	2–15	0
t-BuOOH-Co^{+2}, 50	3.4 ± 0.1[b]	63.2 ± 1.4	13.5 ± 0.6	18.8 ± 1.0
t-BuOOBz-Cu^+, 64–67	0[c]	56.0 ± 1.4[b]	19.4 ± 1.1	24.6 ± 0.3

[a] Data of Shelton and Henderson, ref. 4. [b] Average of two runs. [c] Less than 1%.

of *t*-butoxy radicals on **1** and in determining what effect, if any, metal ions might have on the isomer distribution, we have examined the reaction of **1** with *t*-butyl peroxybenzoate–cuprous bromide.[5,6] These results, along with our own data for the reaction of *t*-butyl hydroperoxide–cobalt naphthenate, are reported in Table II. As with the autoxidation experiments, attack at the secondary allylic hydrogens predominates.[7] The over-all reactions are outlined in eq. 1 and 2.


(1)


(2)

The reliability of the data in Table II is open to some question. Although the reaction of **1** with *t*-butylperoxybenzoate proceeded readily, the yield and the purity of the product were low. After hydrogenation, the benzoate esters were saponified and the resultant alcohols analyzed as previously described. It is not known to what extent the saponification step may have affected the isomer distribution, or how much significance should be attached to the absence of **4b** from the product.

The hydroperoxide–cobalt reaction gave a much cleaner product. The analytical scheme followed the same pattern except that the mixed peroxide was hydrogenated directly to the saturated alcohols with a sponge nickel catalyst. The results are very similar to those reported by Shelton and Henderson if it is assumed that their analysis for **4c** also included **4e**.

In the cases examined, wherein **1** is subjected to attack by an oxy radical the tertiary hydrogen is decidedly less reactive than the secondary even allowing for the statistical factor of four secondary to one tertiary. This reversal of the normal relative reactivities appears in those cyclic olefins in which the tertiary allylic hydrogen and its associated double bond are not part of the same ring. In Table III are grouped a number of these along with some examples for which the usual reactivities apply.

Table III

Autoxidation of Cyclic Olefins

Secondary attack olefin	Tertiary attack olefin
1	**9**[a,b]
5[c]	
6[d]	**10**[a]
7[b,e]	**11**[f]
8[g]	**12**[h]

[a] L. Bateman, *Quart. Rev.* (London), **8**, 147 (1954). [b] J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950). [c] A. Blumann and O. Zeitschel, *Ber.*, **47**, 2623 (1914); G. Widmark, *Arkiv Kemi*, **11**, 211 (1957); *Chem. Abstr.*, **52**, 1107 (1958); E. E. Royals and S. E. Horne, Jr., *J. Am. Chem. Soc.*, **77**, 187 (1955). [d] J. Moulines and R. Lalande, *Bull. soc. chim. France*, 1481 (1960). [e] H. Hock and S. Lang, *Ber.*, **75**, 300 (1942). [f] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 409; H. Hock and F. Depke, *Ber.*, **84**, 356 (1951). [g] V. F. Belyaev and L. V. Kovalev, *Uch. Zap. Belorussk. Gos. Univ. Ser. Khim.*, **29**, 266 (1956); *Chem. Abstr.*, **54**, 7582, (1960). [h] A. G. Davies and J. E. Packer, *Chem. Ind.* (London), 1165 (1960).

These differences in reactivity may stem from the transition state requirement that, for maximum overlap of the developing radical with the π-orbitals of the double bond, the carbon–hydrogen bond to be broken be directed axially to the plane of the double bond. When the double bond and its allylic carbon are not part of the same ring this requirement results in loss of a degree of rotational freedom.[8] Hydrogen–hydrogen interactions between the vinyl hydrogens and those of the substituents on the allylic carbon are at a maximum in this conformation.[9] Both these factors would

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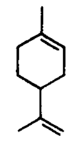
(5) M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).

(6) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

(7) The fact that the *t*-butoxy radical reacts with a surprising degree of selectivity may indicate a complex between the *t*-butoxy radical and the metal ion. Such a complex has been proposed to account for the abnormally high isotope effect for the hydrogen-abstraction step in a similar system [D. B. Denney, D. Z. Denney, and G. Feig, *Tetrahedron Letters*, **No. 15**, 19 (1959)].

(8) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

(9) J. A. Meyer, V. Stannett, and M. Szwarc, *ibid.*, **83**, 25 (1961).



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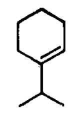

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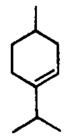

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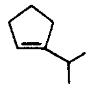

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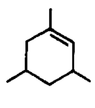

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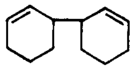

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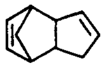

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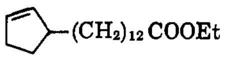

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raise the energy of the transition state for abstraction of the tertiary hydrogen. For systems in which the double bond and its allylic carbon are part of the same ring, attainment of the transition state geometry results in no loss of rotational freedom and no large increase in nonbonded interactions.

Experimental

Materials.—Two samples of 4-vinylcyclohexene were used: Phillips Research grade for the initial experiments and a Humble sample of 99.7% purity for the succeeding runs. Both were percolated over silicic acid and stored under nitrogen prior to use. The solvents employed were *t*-butylbenzene, Phillips Petroleum Company pure grade; benzene, J. T. Baker analyzed reagent; *n*-decane, Matheson Coleman and Bell (b.p. 173–175°), percolated over alumina.

Calibration Compounds.—4-Ethylphenol was hydrogenated at 200° and 1500–1800 p.s.i.g. using Raney nickel catalyst to yield 4-ethylcyclohexanol, b.p. 192° at 768 mm., $n^{27}D$ 1.4601; lit.[10] b.p. 193–196° at 760 mm., $n^{20}D$ 1.4604. Oxidation of this alcohol with potassium dichromate in aqueous sulfuric acid gave 4-ethylcyclohexanone, which forms a semicarbazone, m.p. 171.5–174°, after recrystallization from methylcyclohexane.[11]

3-Ethylcyclohexanone was prepared from cyclohexenone by addition of the Grignard reagent from ethyl bromide and magnesium. It gave a semicarbazone, m.p. 167–174°, lit.[12] m.p. 175°.

2-Ethylcyclohexanone was obtained from Aldrich Chemical Company. It formed a semicarbazone which, after recrystallization from ethanol–water, had m.p. 155–157°, lit.[13] m.p. 163°.

1-Ethylcyclohexanol, prepared from cyclohexanone and the Grignard reagent from ethyl bromide and magnesium, had b.p. 67° at 10 mm.

2-Cyclohexylethanol was prepared by reduction of 4-(2-hydroxyethyl)cyclohexene and had b.p. 85.0° at 4.7 mm.

Oxidation Experiments.—The oxidation reactor consisted of a 500-ml. round-bottomed, four-necked, indented (Morton) flask, equipped with an efficient condenser, thermocouple well, gas inlet tube, and a Teflon-coated, high-speed stirrer. The coated stirrer was used to avoid the corrosion problems and consequent metal contamination observed in other oxidation systems. The apparatus was immersed in an oil bath maintained within ±1° of the desired temperature with a thermoregulating device. Oxygen entered the system through a wet-test meter, passed through the olefin condenser and a Dry Ice–isopropyl alcohol trap, and exited through another wet-test meter. The difference in readings between the inlet and the outlet wet-test meters was used as a measure of oxygen absorption. When the desired conversion had been attained (200 ml. of 1 requires 11 hr. at 60° for absorption of 4.22 l. of oxygen, 12% conversion), the oxygen input was stopped, and the reactor was cooled quickly in an ice–water bath. Conversions were usually *ca.* 12%, but ranged from 6–24%. The cooled oxidation mixture was transferred to a separatory funnel and was washed repeatedly with cold 5% sodium carbonate solution and then with cold 1 *N* sodium hydroxide solution. Acidification of the carbonate extracts produced a small amount (*ca.* 1 g.) of a viscous oil that was not further investigated. The sodium hydroxide extracts were acidified to pH 8.0–8.5 with gaseous carbon dioxide at 0°. The cold solution was extracted repeatedly with ether, the ether was dried with sodium sulfate, and the ether was evaporated. The strongly peroxidic yellow oil recovered (14.64 g., 0.105 mole) was evaporatively distilled at 47–49° and 0.03 mm. to give a nearly colorless oil of 86% purity based on active oxygen determination (iodometric).

In order to determine the isomer distribution in the hydroperoxide mixtures, samples were catalytically hydrogenated to a mixture of saturated alcohols. Thus, a sample of distilled hydroperoxide (1.6575 g., 0.0118 mole) dissolved in 30 ml. of absolute ethanol containing platinum oxide catalyst absorbed 679.8 cc. (0.0303 mole, 86%) of hydrogen. The catalyst was removed by filtration, and the solvent was distilled to yield 1.3352 g. of mixed alcohols. This sample was found to contain 8.9% 1-ethylcyclohexanol (**4b**) by g.l.p.c. analysis.

A sample of the alcohol mixture (1.0564 g., 0.0083 mole) was oxidized with potassium dichromate solution as described by Hussey and Baker[14] to yield 0.8720 g. (0.0069 mole, 83% yield) of mixed ketones and a tertiary alcohol.

Analysis of Ketone and Alcohol Mixtures.—The g.l.p.c. analyses were carried out in two steps. The alcohol mixtures were analyzed on a 2.5-m. column of 40% by weight polypentamethylene adipate on firebrick, operated at 140° and 70 cc./min. of helium. Known mixtures containing the tertiary alcohol were used to obtain calibration data of relative peak area to weight % tertiary alcohol. From this data, the per cent tertiary alcohol in the unknown samples was obtained graphically. Both known and unknown samples were run alternately, under identical conditions and on the same day, to minimize the effect of fluctuations in the operating characteristics of the column.

The ketone mixture was analyzed in much the same way, except that a Perkin-Elmer 300-ft. capillary column coated with Carbowax 20M was used at 130° and 25-lb. helium pressure. Under these conditions the peaks for 1-ethylcyclohexanol and 2-ethylcyclohexanone were sufficiently resolved to permit computation of the peak areas with reasonable accuracy. The remaining two peaks, corresponding to 3- and 4-ethylcyclohexanones, were resolved completely under these conditions. The absence of any other peaks of significant size suggests that the four compounds analyzed comprise the bulk of the sample.

In addition to their g.l.p.c. retention time, the compounds of the mixture were identified by comparing the infrared spectrum of the unknown with that of a synthetic mixture made up to match the g.l.p.c. analysis. The close correspondence of the spectra confirmed the g.l.p.c. assignments. Furthermore, a portion of the ketone mixture was separated by preparative g.l.p.c. Unfortunately, the resolution of the larger column was not sufficient to separate completely the 3- and 4-ethylcyclohexanones. However, the major component was concentrated and a semicarbazone, m.p. 162.5–164°, was prepared. The melting points of the semicarbazones of the isomeric ethylcyclohexanones and of the melting points of their mixtures with the unknown are as follows: 2-ethyl, 155–157°, 138.5–145°; 3-ethyl, 167–174°, 169–171°; 4-ethyl, 171.5–174°, 152–156.5°. Although the semicarbazone is probably not pure, it is evident that the 3-ethylcyclohexanone semicarbazone predominates, in agreement with the g.l.p.c. and infrared data.

Reaction of 1 with *t*-Butyl Hydroperoxide.—The procedure is essentially as described in ref. 4. To a stirred mixture of 108 g. (1 mole) of 1 and 10 g. (~0.1 mole) of *t*-butyl hydroperoxide at 0° was added, under nitrogen, a solution of 0.5 g. of 6% cobalt naphthenate in 0.5 ml. of 1. The mixture was allowed to warm to

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[10] W. Ziegenbein, A. Schäffler, and R. Kaufhold, *Ber.*, **88**, 1906 (1955).

[11] G. I. Kiprianov and A. M. Veitsman [*Ukrain. Khim. Zhur.*, **19**, 662 (1953); *Chem. Abstr.*, **49**, 12320 (1955)] report m.p. 174–175°.

[12] G. F. Woods, P. H. Griswold, Jr., B. H. Armbrecht, D. I. Blumenthal, and R. Plepinger, *J. Am. Chem. Soc.*, **71**, 2028 (1949).

[13] H. E. Ungnade and A. D. McLaren, *J. Org. Chem.*, **10**, 30 (1945).

[14] A. S. Hussey and R. H. Baker, *ibid.*, **25**, 1434 (1960).

room temperature and was heated to 50° for 4.5 hr. The reaction mixture was cooled, diluted with water, and was ether extracted. After having been washed with sodium bicarbonate solution and water and dried with magnesium sulfate, the ether solution was vacuum stripped to give 10.02 g. of crude product. Evaporative distillation at 48–58° and 0.03 mm. gave 4 ml. of colorless distillate and a thick, black residue. The distilled material in 25 ml. of ethanol was hydrogenated with a sponge nickel catalyst at 20° and 100 p.s.i.g. Filtration of catalyst and evaporation of solvent gave 2.78 g. (0.022 mole, ~22%) of a mixture of ethylcyclohexanols. The mixture was analyzed as described before.

Reaction of 1 with *t*-Butyl Peroxybenzoate.—A mixture of 1.004 g. of cuprous bromide and 50.0 ml. of 1 was stirred under helium at 70° while 2.39 g. (0.012 mole) of *t*-butyl peroxybenzoate was added over a 3.5-hr. period. Heating was continued an additional 16.5 hr., after which the mixture was cooled, filtered, washed with saturated sodium bicarbonate solution, then with water, and dried. Vacuum evaporation of unchanged olefin afforded 2.17 g. of residue.

A 2.01-g. sample was hydrogenated in ethanol with platinum oxide catalyst. This material apparently contained some unchanged olefin, since considerably more than the theoretical amount of hydrogen was absorbed (*ca.* 50% excess). The hydrogenation product was evaporatively distilled, then saponified in alcoholic sodium hydroxide. There was obtained 0.502 g. (4.0 mmoles, 36% based on total product) of ethylcyclohexanols. Analysis of the product by g.l.p.c. indicated the presence of small quantities of a number of other materials, as yet unidentified.

Acknowledgment.—The author is indebted to L. C. Jennings for much of the experimental work and to Professors W. E. Doering and R. Pettit for helpful discussions.

1-[*m*-(Ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]-hexafluoropropane and Its Cyclization to a Fluorinated Oxadisila-[3.3]metaparacyclophane

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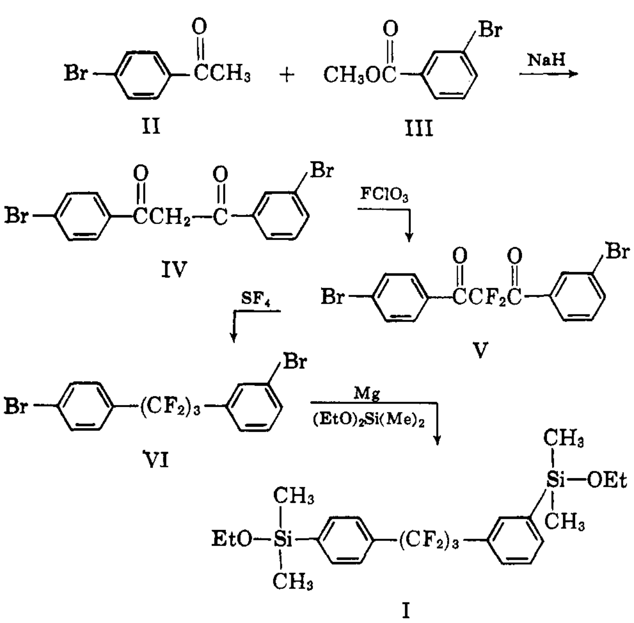
Treatment of a bifunctional Grignard compound, prepared from 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI) with diethoxydimethylsilane, gave 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (I). A sublimate, obtained on heating the polymer of I, was shown to be a fluorinated oxadisila[3.3]metaparacyclophane (VII). To our knowledge, this is the first metaparacyclophane to be reported. Attempts to convert 1,3-bis(*p*-bromophenyl)hexafluoropropane (X) through the bifunctional Grignard compound to 1,3-bis[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (VIII) were not successful.

The synthesis of 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (I) was accomplished through the following sequence.



Condensation of *p*-bromoacetophenone (II) and methyl *m*-bromobenzoate (III) with sodium hydride in benzene gave a 43% yield of 1-(bromophenyl)-3-(*p*-bromophenyl)-1,3-propanedione (IV).

Treatment of IV in pyridine with perchloryl fluoride at −10 to 10° (hazardous!)[2] resulted in a 69% yield of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (V). A 53% yield of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI) was obtained on treatment of V with sulfur tetrafluoride.[3] Formation of a bifunctional Grignard compound from VI, followed by reaction with excess diethoxydimethylsilane, gave a 49% yield of I.

When a solution of I in benzene was refluxed with 50% sulfuric acid, and the benzene solution washed with water and concentrated, a clear tacky polymeric gum was obtained. On heating the gum at 145–155° (0.1 mm.) over a period of 12 hr., a white crystalline sublimate was obtained in 12% yield. Resublimation gave a product, m.p. 80–81.5°, that was homogeneous by v.p.c. The empirical formula $C_{19}H_{20}F_6OSi_2$ was derived from elemental analyses and from the parent peak 434 of the mass spectrum whose base peak 419 represented loss of a methyl group. The observed intensities of the parent +1 and the parent +2 peaks were in accord with those calculated[4] for the given empirical formula. The molecular weight in benzene solution by isothermal distillation was 436. Subsequent determinations gave values of 449 and 496, indicating some repolymerization. The infrared spectrum exhibited the characteristic $Si(CH_3)_2$ band at 7.95 μ, but lacked the ethoxy C–O–Si band at 10.55 μ. The n.m.r. spec-

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(1) Deceased, September 2, 1963.

(2) Although this reaction has been carried out successfully ten times in the course of this work, it is considered to be very dangerous; all due precaution should be taken. The same procedure used in these laboratories for the fluorination of a similar compound, ethyl *p*-fluorobenzoylacetate, resulted in a violent explosion that completely demolished a 0.25-in. Plexiglas "safety" shield.

(3) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

(4) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 9.