West: (a) S_N2 concerted molecular nucleophilic displacement or (b) S_E carbonium ion attack on benzene followed by isomerization of the intermediate t-alkylbenzene. It is evident that the S_N2 reaction, and the isomerization step in (b), both require higher temperatures than the carbonium ion reaction for appreciable conversion to take place. In addition, results obtained in studies of the reaction of isoamylenes with p-xylene (to be reported later) suggest that the reaction proceeds readily via some mechanism other than (b) since steric effects retard initial attack by the bulky t-carbonium ion.

Experimental

Materials.—2-Methyl-2-butene and 3-methyl-1-butene (99+ mole % minimum) were purchased from Phillips Petroleum Company and used as received. t-Pentyl chloride was purchased from the Matheson Company and found to be pure by infrared examination. The benzene used was Fisher ACS and Merck Reagent Grade.

Procedure 1.—A mixture comprising one mole alkylating agent and one mole benzene was added to a stirred mixture comprising four moles benzene, 3.4 moles of n-heptane, and the catalyst saturated with dry HCl. Stirring was continued for 5–10 minutes after the alkylating agent had been added, and the product was permitted to stand for about 10 minutes. The upper layer was separated from the catalyst layer, washed three times with water, stirred several hours with water at about 85 to 95°, dried, stirred with sodium sand at 130–150° for several hours, and distilled. The fractions were analyzed by means of their infrared spectra.[5]

Procedure 2.—The catalyst was added in several portions during the course of the reaction to a stirred mixture comprising 5 moles of benzene and 1 mole of alkylating agent. The products were worked up as in procedure 1.

Procedure 3.—A mixture of 4 moles of benzene and 27 g. of aluminum bromide in a large beaker was saturated with hydrogen bromide gas. At 25° a mixture comprising 1 mole of benzene and 1 mole of 2-methyl-2-butene was *dumped* into the vigorously stirred solution. This was followed by the immediate addition of 400 ml. of water. The estimated time of contact was 1 second. The products were worked up as in procedure 1.

Procedure 4.—Four moles of benzene was introduced under nitrogen pressure into an autoclave (containing 100 g. when employed, of hydrogen fluoride). When required, the boron fluoride gas was then introduced under its own pressure from a 2-liter cylinder. After the temperature had been brought to normal a mixture of 1 mole of benzene and 1 mole of alkylating agent was added with stirring. The product mixture was discharged into a mixture of ice and water. The products were worked up as in procedure 1.

Infrared Standards.—1-Phenyl-2-methylbutane was synthesized by well-known procedures (three steps from benzylmagnesium chloride and methyl ethyl ketone). Grateful acknowledgement is due to Universal Oil Products Company, Riverside, Illinois, for pure samples of 2-phenyl-3-methylbutane, 1-phenyl-3-methylbutane, 1-phenylpentane, 2-phenylpentane, 3-phenylpentane and neopentylbenzene. Pure t-pentylbenzene was obtained from the National Bureau of Standards.

(5) The authors are indebted to F. L. Voelz and F. L. Boys of the Spectrometric Laboratory of Sinclair Research Laboratories, Inc.. for the infrared absorption analyses.

[Contribution from the Department of Chemistry, University of Vermont]

Oxidation of Hindered Phenols. IV. Stable Phenoxy Radicals

By Clinton D. Cook, David A. Kuhn and Peter Fianu

Received October 5, 1955

Stable phenoxy radicals are produced by the alkaline ferricyanide oxidation of 2,6-di-t-alkyl-4-alkoxy and -4-t-alkyl phenols. Properties of these radicals and of peroxides derived from them are reported.
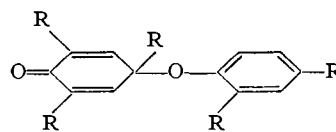
We have suggested[1] that requirements for the formation of a stable mononuclear phenoxy radical are that the *ortho* and *para* positions be substituted by groups sufficiently large to prevent nuclear dimerization and that these groups must not have α-hydrogen atoms. This suggestion was based on the fact that 2,4,6-tri-t-butylphenol (I) is oxidized to 2,4,6-tri-t-butylphenoxy, a relatively stable radical,[1,2,2a,2b] and that 2,6-di-t-butyl-4-methylphenoxy rearranges to the corresponding benzyl radical and then dimerizes.[1]

We have now found that, similar to 2,4,6-tri-t-butylphenol, 2,4,6-tri-t-amylphenol (II) and 2,6-di-t-butyl-4-dimethylethoxymethyl (IX) and -4-dimethylmethoxymethyl (VIII) phenols are readily oxidized by alkaline ferricyanide or lead dioxide to produce the corresponding phenoxy radicals X. Like 2,4,6-tri-t-butylphenoxy, these radicals are of an intense blue color. Similar oxidation of 2,6-di-t-butyl-4-methoxy (V),[3] -4-ethoxy (VI), and -4-t-butoxy-

(1) C. D. Cook, N. G. Nash and H. R. Flanagan, This Journal, **77**, 1783 (1955).

(2) C. D. Cook and R. C. Woodworth, *ibid.*, **75**, 6242 (1953).

(2a) E. Müller and K. Ley, *Ber.*, **87**, 922 (1954).

(2b) E. Müller, K. Ley and W. Kiedaisch, *ibid.*, **87**, 1605 (1954).

(3) While this work was in progress Müller and Ley, (*Ber.*, **88**, 601 (1955)) published a discussion of the 2,6-di-t-butyl-4-methoxyphenoxy radical.

phenols (VII) and of 2,6-di-t-amyl-4-methoxy (IV) and -4-t-amyloxyphenols (III) gives bright red phenoxy radicals.

As compared to tri-t-butylphenoxy, 2,4,6-tri-t-amylphenoxy appears to disproportionate rather readily. While rate measurements were erratic, a rough indication of the rate is given by the fact that an 0.01 M solution of this radical underwent 70% decomposition in an hour. Study of this phenomenon is complicated by the difficulty of establishing the purity of 2,4,6-tri-t-amylphenol (II), a high boiling liquid which appears to dealkylate very readily.

Müller and co-workers[2b] have reported the formation of 2,4,6-tri-t-butylphenol on disproportionation of 2,4,6-tri-t-butylphenoxy. In addition to the phenol we have found that the disproportionation produces isobutylene and at least two dimeric products. The elemental analysis and infrared and ultraviolet spectra of one of the dimeric products are suggestive of a structure such as XI


XI, R = t-butyl

TABLE I

PROPERTIES OF OXIDATION PRODUCTS OF 2,4,6-TRI-SUBSTITUTED PHENOLS

R	R'	M.p. or b.p., °C.	Color	Max. vis-ible, mμ	I.r. absorption, cm.^-1	M.p., °C.	Calcd. C	Calcd. H	Found C	Found H	U.v. max, mμ	εmax × 10^-4
I	t-Butyl	t-Butyl	M.p. 130–131	Blue	625	1573 (strong) 1507 (medium)	Reported in ref. 2					242	25.8
II	t-Amyl	t-Amyl	M.p. +0.8 94–96 at 0.08 mm.	Blue		1573 (strong) 1507 (medium)		78.94	11.04	79.11	11.20	241	25.4
III	t-Amyl	t-Amyloxy^a	B.p. 118–119 at 0.02 mm.	Red			82–84 dec.	75.17	10.51	75.14	10.37	235	20.4
IV	t-Amyl	Methoxy^a	Liq. at r.t.	Red									
V	t-Butyl	Methoxy^b	M.p. 103.5–104.5	Red	535	1590 (strong) 1509 (medium)	110–111 reported* 114–115	71.68	9.22	71.78	9.17	230	21.3
VI	t-Butyl	Ethoxy	M.p. 83–84	Red	530	1590 (strong) 1509 (medium)	125–126	72.43	9.51	72.39	9.42		
VII	t-Butyl	t-Butoxy^a	M.p. 99–100	Red	538	1590 (strong) 1509 (medium)	109–109.5 dec.	73.68	9.96	73.66	9.75	232	15.6
VIII	t-Butyl	Dimethylmethoxymethyl^c		Blue	637								
IX	t-Butyl	Dimethylethoxymethyl^c		Blue									

a C. D. Cook, R. C. Woodworth and P. Fianu, THIS JOURNAL, **78**, in press (1956).   *b* C. D. Cook, R. G. Inskeep, A. W. Rosenberg and E. Curtis, Jr., *ibid.*, **77**, 1672 (1955).   *c* C. D. Cook and B. E. Norcross, *ibid.*, **78**, in press (1956).

The *p*-alkoxyphenoxy radicals appear to be considerably more stable. Thus on standing overnight at room temperature, 0.001 *M* solutions showed less than 1% decomposition.

These phenoxy radicals react readily with oxygen to produce the corresponding bis-cyclohexadienone peroxides (eq. 1)

(1)

R = *t*-alkyl group
R' = *t*-alkyl, alkoxy or dimethylalkoxymethyl group
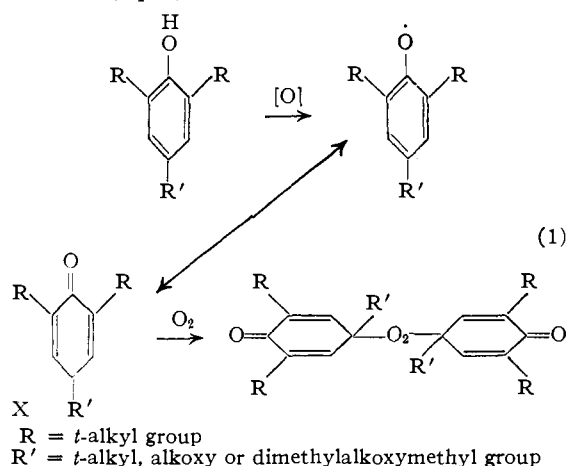
The properties and analytical data on the phenols, phenoxy radicals and peroxides are shown in Table I.

Infrared spectra of the phenoxy radicals show a characteristic absorption which, as might be expected from the canonical forms, resembles a weakened carbonyl absorption[4] (see Table I). This, the mode of formation, the intense color and the reaction with oxygen were taken as evidence for the free radical character of the oxidation products. By magnetic susceptibility measurements, Chu and Yu[5] have shown the presence of an unpaired elec-

tron in 2,6-di-*t*-butyl-4-methoxy, -4-ethoxy, and 4-*t*-butoxyphenoxys and in 2,4,6-tri-*t*-butylphenoxy.

Mobile equilibria are set up between the various radicals and the corresponding phenols[6] (eq. 2).

(2)
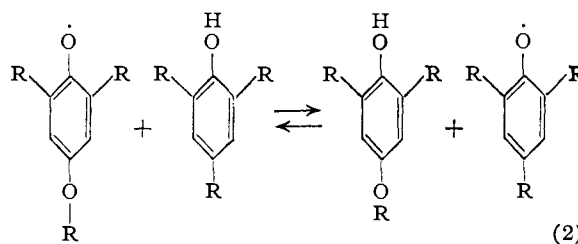
The absorption spectra shown in Fig. 1 illustrate the attainment of such an equilibrium. Since difficulties were encountered in obtaining accurate values for the extinction coefficients, little quantitative significance can be attached to the curves. However, the results indicate equilibrium constants in the order of 10^{-1} to 10^{-3} for the reaction as written. The oxidation potential of 2,6-di-*t*-butyl-4-methoxyphenoxy is apparently somewhat greater than that of diphenoquinone (approx. 0.95) since an excess of the latter is necessary to produce a pink color in a solution of 2,6-di-*t*-butyl-4-methoxyphenol (V). Diphenoquinone does not appreciably oxidize 2,4,6-tri-*t*-butylphenol (I); the corresponding phenoxy radical is rapidly reduced by *p,p'*-dihydroxydiphenyl.

The facile attainment of these equilibria may be helpful in explaining the fact that mixtures of hindered phenols (as, for example, 2,6-di-*t*-butyl-4-methyl- and -4-methoxyphenols) frequently prove to be better autoxidation inhibitors than either of

(4) R. G. Inskeep, C. D. Cook and D. A. Kuhn, unpublished work. See also ref. 2a and 3.

(5) T. L. Chu and S. C. Yu, personal communication.

(6) Müller, *et al.*,[8] have reported that tri-*t*-butylphenoxy will oxidize 2,6-di-*t*-butyl-4-methoxyphenol to the corresponding phenoxy radical. They did not, however, note the reversibility of this reaction.
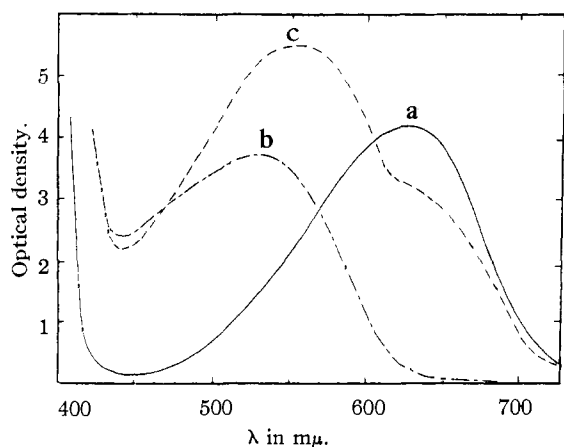
Fig. 1.—a, approx. 0.0015 M solution of 2,4,6-tri-t-butyl-phenoxy; b, approx. 0.003 M solution of 2,6-di-t-butyl-4-ethoxyphenoxy; c, solution which at time of mixing was approx. 0.002 M in 2,4,6-tri-t-butylphenoxy and 0.001 M in 2,6-di-t-butyl-4-ethoxyphenol.

the constituents. Further studies on these equilibria are in progress.

Phenoxy radicals frequently have been postulated as intermediates in the reactions of phenols with peroxides.[7,8] We have found that when benzoyl peroxide is decomposed in the presence of 2,4,6-tri-t-butylphenol or 2,6-di-t-butyl-4-methoxy- or -4-t-butoxyphenols, appreciable concentrations of the corresponding phenoxy radicals are produced. This is of particular interest since recent kinetic evidence on autoxidation inhibition by Boozer and Hammond[9,10] seems best explained on the basis of a peroxide radical–phenol complex rather than on the basis of free phenoxy radicals. Whether or not such a complex intervenes in the present case is not yet known.

Acknowledgments.—We are grateful to the Research Corporation for a Frederick Gardner Cottrell grant and to Dr. Richard G. Inskeep for the infrared spectra. We are indebted to Dr. T. L. Chu for keeping us informed of the progress of his studies on the magnetic susceptibilities of these radicals.

Experimental

Preparation of 2,4,6-Tri-t-amylphenol.—This phenol was prepared by a modification of the method of Stillson, Sawyer and Hunt.[11,12] A solution of 94 g. (1 mole) of phenol and 5 ml. of concentrated sulfuric acid was cooled to below 5° and 240 g. (3.42 moles) of trimethylethylene[13] was added dropwise over a period of 10 hours. The mixture was shaken with 200 ml. of Claisen solution (350 g. of potassium hydroxide in 250 ml. water, diluted to 1 liter with methanol) and then with five 100-ml. portions. The benzene layer was washed with water, the benzene evaporated

(7) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949); 388 (1951).

(8) T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).

(9) C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3861 (1954).

(10) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3268 (1955).

(11) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *ibid.*, **67**, 303 (1945).

(12) Dr. Stillson very helpfully provided further details in a personal communication.

(13) J. F. Norris and R. Reuter, THIS JOURNAL, **49**, 2624 (1927).

and the residue distilled through a 24-in. Vigreux column at 0.08 mm. A yield of 48 g. (16%) of 2,4,6-tri-t-amylphenol, boiling at 94–96°, was obtained. A cooling curve, after one refractionation, gave a sharp break at 0.8°. Further fractionations gave no noticeable improvement in purity. It was found that prolonged heating during fractionation led to partial dealkylation.

The first fraction (b.p. 85–86° at 0.08 mm.) from the distillation of the alkylation mixture gave, upon oxidation with alkaline ferricyanide, shiny purple crystals, m.p. 235–236°. This compound is believed to be 3,3′,5,5′-tetra-t-amyldiphenoquinone. Comparison of the ultraviolet and visible absorption spectra with that of 3,3′,5,5′-tetra-t-butyldiphenoquinone supports this view. The maxima reported[14] for the t-butyl derivative are at 251, 260, 269 and 420 mμ with extinction coefficients of 4740, 5480, 4920 and 70,800, respectively. For the t-amyl derivative we found maxima at 252, 262, 272 and 425 mμ with extinction coefficients of 4700, 5100, 4400 and 70,000, respectively. *Anal.* Calcd. for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41. Found: C, 82.79; H, 10.17.

Preparation of 2,6-Di-t-butyl-4-ethoxyphenol.—A solution of 6 g. of potassium hydroxide and 1 g. of sodium hydrosulfite in 50 ml. of boiled water was flushed briefly with oxygen-free nitrogen. To this solution was added a solution of 20 ml. of diethyl sulfate and five of crude 2,6-di-t-butylhydroquinone (footnote a and b of Table I) in 35 ml. of acetone. The system was vigorously stirred for 3 hours under a nitrogen atmosphere. After washing twice with 10% sodium hydroxide the acetone layer was evaporated to dryness to give a 70% yield of crude 2,6-di-t-butyl-4-ethoxyphenol. After two recrystallizations from petroleum ether (b.p. 35–60°) the white product melted at 83–84°.[15]

Preparation of Other Phenols. (a).—The 2,6-di-t-amyl-4-methoxyphenol was prepared by the dimethyl sulfate alkylation of 2,6-di-t-amylhydroquinone (footnote a of Table I). The infrared spectrum of the resulting viscous liquid showed only the hindered hydroxyl group and suggested a relatively pure compound. The product was therefore used without further purification.

(b).—The 2,6-di-t-butyl-4-t-butoxy and 2,6-di-t-amyl-4-t-amyloxyphenols were prepared by thermal decomposition of the corresponding bis-cyclohexadienone peroxides (footnote a of Table I).

(c).—Addition of methanol and ethanol to 2,6-di-t-butyl-4-isopropenylquinone methide gave 2,6-di-t-butyl-4-dimethylmethoxymethyl and -4-dimethylethoxymethylphenols (footnote c of Table I).

Preparation of the Radicals.—Solutions of the radicals for visible spectra were prepared by oxidizing the phenols with a large excess of alkaline ferricyanide under a nitrogen atmosphere. The nitrogen was purified with the sodium-potassium ketyl of benzophenone.[16] The solutions were transferred to Pyrex cuvettes under the nitrogen atmosphere and immediately sealed. A Beckman model D.U. spectrophotometer was used to measure the spectra.

For the infrared spectra, oxygen-free solutions of the phenols were shaken with lead dioxide and then centrifuged. Using a hypodermic syringe they were then rapidly transferred to the cell. Spectra were recorded on a Perkin-Elmer model 112 spectrometer.

Preparation of the Peroxides.—Benzene solutions of the phenols were stirred with an excess of alkaline ferricyanide solution while oxygen was bubbled through the system. When the color of the radical disappeared, the benzene layer was separated and evaporated to dryness. The light yellow products were recrystallized from ethanol. It was necessary to perform these recrystallizations rapidly to minimize decomposition and thus insure pure products. Yields were in the order of 90%.

Infrared spectra[4] on these peroxides showed the characteristic conjugated carbonyl bond in the region of 1640–1690 cm.$^{-1}$. The ultraviolet spectra were similar, although the alkoxy groups caused a displacement of the maximum towards shorter wave lengths (see Table I).

(14) W. J. Detroit and H. Hart, *ibid.*, **74**, 5215 (1952).

(15) The product was identical with a specimen kindly provided by Dr. L. J. Kitchen and prepared by the isobutylene alkylation of p-ethoxyphenol. Dr. Kitchen obtained a melting point of 84.5–85.5° on this material.

(16) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1941, p. 396.

Disproportionation of Tri-*t*-butylphenoxy.—When concentrated (*ca.* 20%) solutions of tri-*t*-butylphenoxy in petroleum ether were cooled to −70° (Dry Ice and acetone) blue crystals separated from the mixture. These crystals maintained their blue color for several weeks at room temperature, although they gradually turned yellow. On heating they decomposed vigorously at around 80°. A gas, having the characteristic odor of isobutylene, was evolved. Vacuum distillation of part of the decomposition product gave approximately a 50% yield of 2,4,6-tri-*t*-butylphenol, identified by its melting point and infrared spectrum. Careful fractional recrystallization of the decomposition product from methanol and water gave a yellow compound I, m.p. 148–149° in low yield. The infrared spectrum of this compound shows the absence of a hydroxyl group (no absorption in the region of 3300–3700 cm.$^{-1}$) and the presence of a conjugated carbonyl (strong absorption at about 1688 cm.$^{-1}$). The ultraviolet spectrum shows a maximum at 287 mμ, ϵ_{max} 3.7 × 10^3, similar to phenyl ethers (footnote *b* of Table I). *Anal.* Calcd. for C$_{32}$H$_{50}$O$_2$(I): C, 82.34; H, 10.80; mol. wt., 466.72. Found: C, 82.51; H, 10.53; mol. wt. (Rast, micro), 472.

In an attempt to simplify the separation problem, a reaction was run under conditions where the regenerated 2,4,6-

tri-*t*-butylphenol would be reoxidized and converted to disproportionation product. In an apparatus equipped with a reflux condenser and mercury trap, a solution of 10 g. of the phenol in 50 ml. of benzene was stirred with a solution of 10 g. of potassium hydroxide and 50 g. of potassium ferricyanide in 150 ml. of water. The temperature was maintained at 70° for five days. At the end of this period the system had no detectable blue color. Evaporation of the benzene left an orange-yellow, viscous residue. Attempted recrystallizations from methanol and water produced a mixture of crystals which we were unable to satisfactorily separate. The infrared spectrum of this mixture indicated that it contained approximately 50% of dimer XI, that the other constituent(s) also had a carbonyl and that no hydroxyl group was present in the mixture. The carbon–hydrogen analysis of the mixture suggests that the other product is a dimer which has lost two *t*-butyl groups.

Anal. Calcd. for C$_{28}$H$_{41}$O$_2$: C, 82.10; H, 10.09. Found for the mixture: C, 82.19; H, 10.13.

Analytical.—All carbon–hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory.

Burlington, Vermont

Small-Ring Compounds. XIII. The Mechanism of Racemization of Optically Active 2,4-Dichloro-3-phenylcyclobutenone[1]

By Erwin F. Jenny[2] and John D. Roberts

Racemization of optically active 2,4-dichloro-3-phenylcyclobutenone has been shown to involve reversible formation of (1-phenyl-2-chloroethenyl)-chloroketene. 2,4-Dichloro-3-phenyl-3-butenoic acid yields 2,4-dichloro-3-phenylcyclobutenone on treatment with acetic anhydride.

2,4-Dichloro-3-phenylcyclobutenone[3] (I) is of considerable theoretical interest since on enolization it would yield 2,4-dichloro-3-phenylcyclobutadienol (II).

$$C_6H_5\text{—}\diamondsuit\text{=}O \rightleftarrows C_6H_5\text{—}\diamondsuit\text{—}OH \quad (1)$$
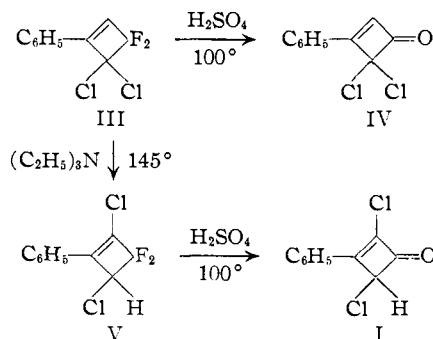
I   II
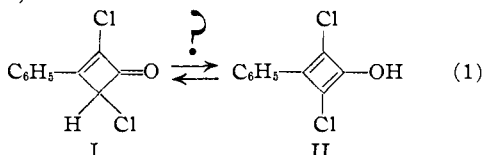
Enolization of I does not occur readily. The compound gives no color with ferric chloride solution and shows no hydroxyl absorption in the infrared.[3] It dissolves in alkali, but acidification yields 2,4-dichloro-3-phenyl-3-butenoic acid and complex products.[3] No reaction was noted in an attempt to convert I to 1-acetoxy-2,4-dichloro-3-phenylcyclobutadiene with isopropenyl acetate in the presence of *p*-toluenesulfonic acid under conditions which have been used successfully to convert other ketones to their enol acetates.[3]

None of the foregoing observations strictly preclude interconversion of I and II, provided the equilibrium constant is suitably small. Formation of II could be definitely excluded if compound I were resolved (it has one asymmetric center) and found not to racemize under any of the conditions which are usually conducive to enolization. It has now been found that partial resolution of I is eas-

ily achieved but that loss of optical activity occurs rather readily on heating in several solvents. The mechanism of this racemization reaction is the subject of the present investigation.

Preparation of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (III) from 1,1-difluoro-2,2-dichloroethylene and phenylacetylene has been described previously.[3] III was transformed to 2,2-dichloro-3-phenylcyclobutenone (IV), 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (V) and I as shown in the equations

$$C_6H_5\text{—}\diamondsuit\text{—}F_2 \xrightarrow[100°]{H_2SO_4} C_6H_5\text{—}\diamondsuit\text{=}O$$

III   IV

$$(C_2H_5)_3N \downarrow 145°$$

$$C_6H_5\text{—}\diamondsuit\text{—}F_2 \xrightarrow[100°]{H_2SO_4} C_6H_5\text{—}\diamondsuit\text{=}O$$

V   I

Rearrangement of III with brucine in place of triethylamine gave optically active V possibly by way of a stereospecific and reversible Menschutkin reaction.

$$C_6H_5\text{—}\diamondsuit\text{—}F_2 \xrightarrow{brucine} (+) \; C_6H_5\text{—}\diamondsuit\text{—}F_2$$

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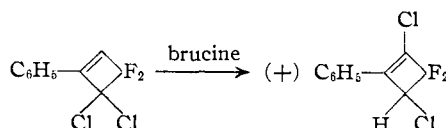
(1) Presented at the 14th National Organic Symposium of the American Chemical Society, Lafayette, Ind., June 14, 1955.

(2) Arthur Amos Noyes Fellow, 1954–1955.

(3) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., This Journal, **75**, 4765 (1953).