

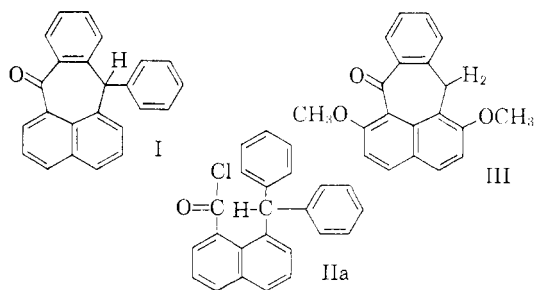
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

peri-Substituted Naphthalenes. II. A Rearrangement Involving a 1,5-Aryl Migration¹BY PETER T. LANSBURY² AND ROBERT L. LETSINGER

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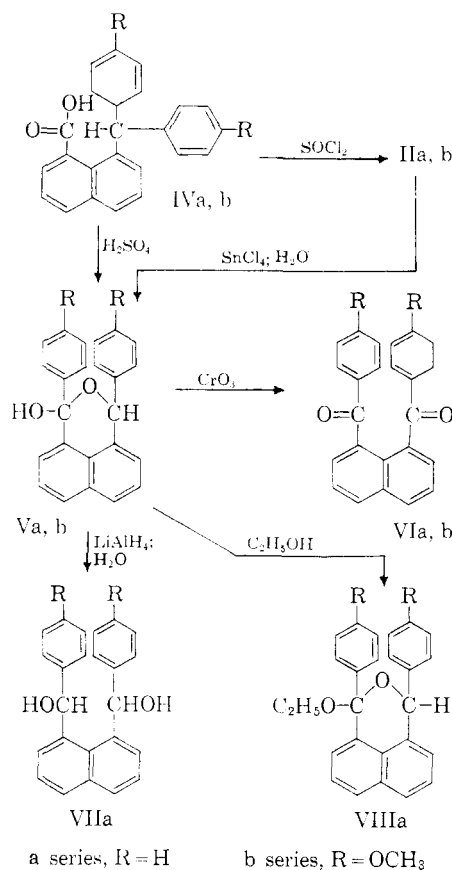
Under Friedel-Crafts conditions 8-benzhydryl-1-naphthoic acid (IVa) isomerizes in high yield to 1-phenylhydroxymethyl-8-benzoylnaphthalene hemiketal (Va). Similarly, 8-(di-*p*-anisylmethyl)-1-naphthoic acid rearranges to a di-*p*-anisyl analog of Va. These reactions involve a 1,5-aryl shift. In concentrated sulfuric acid, 1-hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (IX) isomerizes to Va, a reaction in which a phenyl group and hydrogen exchange positions.

In the process of characterizing a new substance, we needed to prepare compound I. It appeared that this ketone could be obtained by cyclization of 8-benzhydryl-1-naphthoyl chloride (IIa). Although the Friedel-Crafts reaction is less satisfactory for the formation of seven-membered rings,³ numerous examples of somewhat similar closures have been reported. In fact Fieser⁴ obtained a 90% yield of III from 2,7-dimethoxy-1-(2-carboxybenzyl)-naphthalene. Nevertheless, the attempt to prepare I was unsuccessful for the cyclization reaction was superseded by an unusual type of rearrangement. The elucidation of the chemistry of this transformation was the object of the research described in this paper.



8-Benzhydryl-1-naphthoic acid (IVa) was converted to the acid chloride, which in turn, was treated with stannic chloride in carbon disulfide. A vigorous reaction ensued with the formation of an insoluble red complex. Hydrolysis of this complex yielded (90%) a white, crystalline, neutral product (Va) which, however, was not the expected ketone. The analysis corresponded to $C_{24}H_{18}O_2$, an isomer of benzhydrylnaphthoic acid, and the infrared spectrum indicated the presence of OH (2.8μ) and C-O-C (a strong band at 9.7μ)⁵ and the absence of C=O. The key to the structure of Va was provided by oxidation with chromium trioxide, which afforded a 45% yield of 1,8-dibenzoylnaphthalene (VIa) and by reduction with lithium aluminum hydride, which gave 1,8-bis-(phenylhydroxymethyl)-naphthalene (VIIa) (60% yield). These data show that Va must be the hemiketal of 1-phenylhydroxymethyl-8-benzoylnaphthalene. Under the Friedel-Crafts conditions, therefore, a phenyl group migrated from car-

bon at an 8-position to carbon at a 1-position of naphthalene.



8-Benzhydryl-1-naphthoyl chloride reacts with methanol⁶ and ethanol to give the corresponding esters, showing that the rearrangement described above must have occurred during the reaction with stannic chloride and not during the reaction with thionyl chloride.

It was found that IVa could also be converted directly to Va by the action of sulfuric acid. Since IVa itself can be prepared by isomerization of hemiketal IX in formic acid,⁷ it appeared that sulfuric acid might isomerize IX to Va. This reaction, which involves an interchange of hydrogen and phenyl, did indeed go. A 67% yield of Va was obtained by dissolving IX in concentrated sulfuric acid and subsequently diluting the mixture with water.

(6) G. Wittig and H. Petri, *Ber.*, **68**, 924 (1935).

(7) R. L. Letsinger and P. T. Lansbury, *THIS JOURNAL*, **81**, 935 (1959).

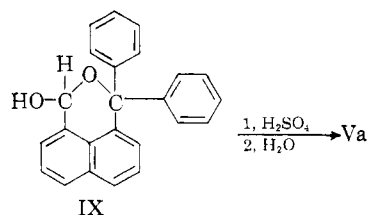
(1) For a preliminary account of this work see R. L. Letsinger and P. T. Lansbury, *THIS JOURNAL*, **78**, 2648 (1956).

(2) National Science Foundation Pre-doctoral Fellow, 1955-1956.

(3) W. S. Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 114.

(4) L. F. Fieser, *THIS JOURNAL*, **55**, 4977 (1933).

(5) All the compounds in this and the preceding paper to which a naphthopyran structure was assigned exhibited very strong absorption between 9.7 and 9.8μ .



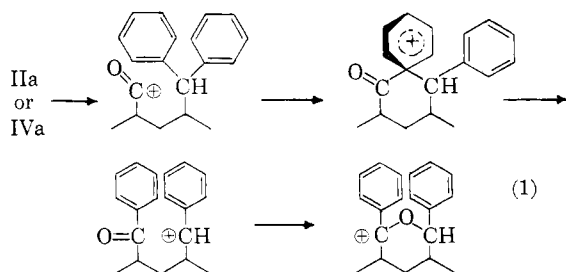
Compound Va reacted with ethanol in the presence of a small amount of sulfuric acid to give a ketal (VIIIa) isomeric with ethyl 8-benzhydryl-1-naphthoate and the ethyl acetal of IX. Melting point data on these isomers and on compounds IVa, Va, and IX are summarized in Table I.

TABLE I
MELTING POINTS OF $C_{24}H_{18}O_2$ ISOMERS AND DERIVATIVES

R			
H	165.5-167	231-231.5	137-137.5
CH ₃	183-184	167-167.5
C ₂ H ₅	197.5-198.5	119-119.5	203.5-204.5

Infrared spectral data confirm the fact that all the various isomers were different substances. In addition, IX and Va differed markedly in reactivity. The contrast in behavior of these compounds in acid solutions has been noted. With nucleophilic agents the reactivity seems to be reversed, since hemiacetal IX was not reduced by excess lithium aluminum hydride⁷ whereas hemiketal Va was reduced. Furthermore, phenyllithium reacted with Va, producing $C_{30}H_{24}O_2$, but it did not noticeably affect the ethyl acetal of IX. Compound Va and IX also differed in their reactivity toward 2,4-dinitrophenylhydrazine; Va yielded a derivative but IX did not.

The mechanistic features of the rearrangement may reasonably be represented by 1. According to this, an acyl carbonium ion attacks the near-by

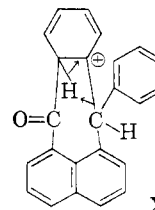


phenyl ring, forming a cyclic intermediate or transition state. Following scission of the carbon-carbon bond, the newly formed ion adds to oxygen of the carbonyl group to give a more stable ion, which yields Va on addition of water. An intramolecular pathway of this type is much more likely than an intermolecular process since stannic chloride, though an effective agent for effecting intramolecular acylation,³ is generally not sufficiently reactive to bring about intermolecular Friedel-Crafts reactions with benzene.⁸ Furthermore, as a model for an intermolecular reaction we

(8) G. Stadnikoff and A. Baryochewa, *Ber.*, **61**, 1996 (1928).

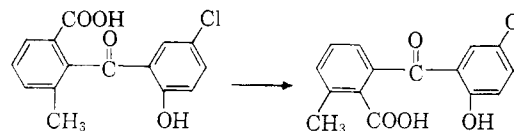
subjected a mixture of benzoyl chloride and triphenylmethane to the action of stannic chloride in carbon disulfide. Although the time of reaction was much longer (15 hours as compared to 1.5 hours for the reaction involving II) no evidence for a reaction was found. No carbonyl compounds could be detected and 92% of the triphenylmethane was recovered.

An alternate possibility for the reaction would involve attack of the acylium ion on an *o*-position of the neighboring phenyl group (see X).



As a test of this mechanism, the acid chloride of 8-(di-*p*-anisylmethyl)-1-naphthoic acid (IIb) was prepared and treated with stannic chloride in carbon disulfide. An 87% yield of a rearranged hemiketal (Vb) was obtained. Oxidation with chromium trioxide yielded 1,8-di-*p*-anisoylnaphthalene (VIb) in agreement with sequence 1. Reaction *via* an intermediate of type X would have given 1-*p*-anisoyl-8-*m*-anisoylnaphthalene. It is therefore clear in this case that the migrating aryl group undergoes detachment and attachment at the same ring carbon atom.

These rearrangements appear to be the only examples of a reaction which involves a 1,5-aryl shift between carbon atoms. A related reaction is the Hayashi rearrangement of substituted *o*-benzoylbenzoic acids.⁹ Normally *o*-benzoylbenzoic acids cyclize in sulfuric acids to give anthraquinones; however, in certain cases where the aryl group is activated, as in 2-[2-hydroxy-5-chlorobenzoyl]-3-methylbenzoic acid, 1,4-aryl migration takes place.



A 1,4-type rearrangement was also reported by Winstein and co-workers, who found that formolysis of 4-methyl-4-*p*-anisoyl-1-pentyl *p*-bromobenzene-sulfonate yields 1,1-dimethyl-7-methoxytetralin.¹⁰ Finally, partial conversion of the diazonium salt of 9-aminophenyl-9-fluorenone to tribenzotropone involves a 1,3-aryl shift.¹¹

Experimental Section

Rearrangement of 8-Benzhydryl-1-naphthoic Acid (IVa)
(a).—One gram of IVa¹² was warmed under reflux for 30 minutes with 10 ml. of thionyl chloride, 20 ml. of absolute ether and two drops of pyridine. Excess thionyl chloride and

(9) (a) M. Hayashi, *J. Chem. Soc.*, 2516 (1927); (b) R. Sandin, R. Melby, R. Crawford and D. McGreer, *THIS JOURNAL*, **78**, 3817 (1956); (c) M. S. Newman and K. G. Ihrman, *ibid.*, **80**, 3652 (1958); (d) see J. W. Cook, *J. Chem. Soc.*, 1472 (1932), for a similar type of rearrangement.

(10) S. Winstein, R. Heck, S. Lapporte and H. Baird, *Experientia*, **12**, 138 (1956).

(11) M. Stiles and A. J. Libbey, *J. Org. Chem.*, **22**, 1243 (1957).

(12) W. E. Bachmann and E. Chu, *THIS JOURNAL*, **58**, 1118 (1936).

solvent were then taken off at a water aspirator, the crude acid chloride taken up in benzene, and the benzene removed at reduced pressure. The resulting white solid was dissolved in 10 ml. of carbon disulfide, and a solution of 1.2 ml. of stannic chloride in 10 ml. of carbon disulfide was added. The mixture was refluxed for 90 minutes, then cooled, and the carbon disulfide decanted and replaced with ether. The complex was hydrolyzed by pouring onto a mixture of ice and concentrated hydrochloric acid, with stirring to break up the lumps. The ether layer was washed successively with dilute hydrochloric acid, water, dilute sodium hydroxide solution (no acidic products were obtained on acidifying this extract) and twice with water. After drying over sodium sulfate, a portion of the ether solution was evaporated and the residue treated with petroleum ether (b.p. 60–70°) and allowed to cool. Feathery white crystals, m.p. 136.5–137.5°, of hemiketal Va separated. Recrystallization from benzene–petroleum ether gave 0.90 g. (9%) of pure Va, m.p. 137–137.5°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.12; H, 5.21.

(b).—Compound IVa (0.50 g.) was heated on a steam-bath for two hours with 16 ml. of sulfuric acid and 4 ml. of water (not all of the solid went into solution). The orange mixture was then cooled, poured onto crushed ice, and the precipitate taken up in ether. Extraction with 10% sodium carbonate solution and acidification of the extract gave 0.30 g. of IVa (60% recovery). After the ether layer was washed and dried over sodium sulfate, it was partially evaporated and treated with petroleum ether (b.p. 60–70°). The residual solid was recrystallized from chloroform–petroleum ether, giving 0.10 g. (20%) of colorless, crystalline Va, m.p. 136.5–137°, which was identical with the product from the stannic chloride reaction.

Oxidation of 1-Phenylhydroxymethyl-8-benzoylnaphthalene Hemiketal (Va).—A mixture of 0.20 g. of Va, 0.10 g. of chromium trioxide and 10 ml. of glacial acetic acid was warmed on a steam-bath for one hour and then diluted with ice-water. The precipitate was separated by filtration, washed with water, and recrystallized from acetone–ethanol (with Norit treatment), yielding 0.09 g. (45%) of 1,8-dibenzoylnaphthalene, m.p. 188.5–189.5° (lit.¹² m.p. 189–190°). The product gave no melting point depression when mixed with an authentic sample of the diketone prepared by oxidation of 1,2-diphenyl-1,2-acenaphthenediol,¹² and the infrared spectra of the two samples were superimposable.

Reduction of Va.—A mixture of 0.20 g. of Va, 0.15 g. of lithium aluminum hydride and 25 ml. of ether was refluxed overnight, and the reaction mixture was then decomposed with 20% sodium carbonate solution. The ether solution was worked up as described for the reduction of 1,8-dibenzoylnaphthalene,⁷ yielding 0.12 g. (60%) of 1,8-bis-(phenylhydroxymethyl)-naphthalene, m.p. 199.5–200.5°, which gave no melting point depression when mixed with the diol prepared from 1,8-dibenzoylnaphthalene.⁷ The infrared spectra of these samples of VIIa were identical.

Preparation of Va by Isomerization of IX.¹³—1-Hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (IX) (0.300 g.) was dissolved in 30 ml. of cold, concentrated sulfuric acid. After standing for 45 min. at 0°, the deep red-brown solution was poured onto ice and worked up in the usual way. No acidic materials were obtained on acidification of the base extract. Evaporation of the neutral ether layer left 0.20 g. (67%) of the hemiketal rearrangement product (Va), m.p. 132–137°. One recrystallization gave the pure hemiketal, identical in melting point and infrared spectrum with the product obtained from the stannic chloride reaction of 8-benzhydryl-1-naphthoyl chloride. A mixed melting point of the two samples showed no depression.

Esters of 8-benzhydryl-1-naphthoic acid were obtained by treating the acid chloride IIa with methanol and ethanol, a procedure used by Wittig and Petri for preparation of methyl 8-benzhydryl-1-naphthoate.⁸ From 0.6 g. of benzhydrylnaphthoic acid was obtained 0.48 g. (77%) of the methyl ester, m.p. 167–167.5° (lit.⁸ 168°). Likewise from 0.50 g. of benzhydrylnaphthoic acid was obtained a 92% yield of ethyl 8-benzhydrylnaphthoate, m.p. 119°.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 84.79; H, 5.87.

Both esters showed strong carbonyl bands at 5.80 μ and no absorption in the hydroxyl region.

(13) This experiment was carried out by W. J. Vullo.

Reaction of Va with Ethanol.—A solution of 0.30 g. of Va and two drops of sulfuric acid in 10 ml. of absolute ethanol was refluxed for 30 minutes and then treated with sufficient 5% sodium bicarbonate solution to render the mixture alkaline. Further dilution with water and cooling caused the ketal to precipitate. On recrystallization from ethanol–acetone, 0.23 g. (71%) of the ethyl ketal (VIIa), m.p. 188–198°, was obtained. After three more recrystallizations an analytical sample was obtained which melted at 203.5–204.5°. The infrared spectrum showed high intensity bands at 9.4, 9.7 and 9.9 μ and no absorption in the hydroxyl region.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.43; H, 6.00.

Reaction of Va with 2,4-Dinitrophenylhydrazine.—A solution of Va and 2,4-dinitrophenylhydrazine reagent¹⁴ in ethanol was refluxed for 30 minutes. On dilution with water an orange solid separated. After recrystallization from acetone–ethanol, it was pale yellow and melted at 215–218° dec.

Anal. Calcd. for $C_{30}H_{22}O_5N_4$: N, 10.81. Found: N, 10.75.

Reaction of Va with Phenyllithium.—To 0.25 g. of the hemiketal (Va) in 20 ml. of ether was added 10 ml. of 1.21 M phenyllithium. After the resulting solution had refluxed for 8 hours, it was hydrolyzed by addition of water. The ether layer was separated, washed with water, dried over sodium sulfate, and partially evaporated. On addition of petroleum hexane 0.13 g. (42%) of chunky, white crystals, m.p. 214–218°, settled out. The filtrate on standing overnight yielded an additional 0.10 g. of material which melted at 160–175°. The first crop of crystals was recrystallized several times from ethanol, yielding an analytical sample which melted at 215–217°. The infrared spectrum (potassium bromide pellet) showed strong bands at 2.9, 8.5 and 9.5 μ , among others. From the nature of the reaction and the analysis of the product, it is highly probable that the product is 1-phenylhydroxymethyl-8-(diphenylhydroxymethyl)-naphthalene.

Anal. Calcd. for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.59; H, 5.41.

Effect of Phenyllithium on 1-Ethoxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran.—A solution containing 10 ml. of 0.72 M phenyllithium and 0.20 g. of the ethyl acetal derivative of IX⁷ was refluxed for 30 minutes and allowed to stand overnight at room temperature. The reaction mixture was hydrolyzed with water and dried over sodium sulfate. Partial evaporation of the ether and dilution with petroleum ether yielded 0.17 g. (85% recovery) of white crystals, m.p. 186–191°. The infrared spectrum of this material was the same as that of the starting compound.

Rearrangement of 8-(Di-*p*-anisylmethyl)-1-naphthoic Acid (IVb).—A solution containing 1.00 g. of IVb¹² and 0.3 ml. of thionyl chloride in 20 ml. of absolute ether was allowed to stand for an hour at room temperature (it was found that a dark, tarry product resulted when IVb was warmed in a large excess of thionyl chloride); then the excess thionyl chloride and ether were distilled. Residual thionyl chloride was removed by dissolving the residue in benzene and removing the benzene under reduced pressure.

To the acid chloride was added 10 ml. of carbon disulfide and a solution of 1.0 ml. of stannic chloride in 10 ml. of carbon disulfide. A vigorous reaction ensued with the formation of an insoluble complex. The mixture was heated for an hour; then it was worked up in the same manner as in the preparation of Va. The yield of the hemiketal Vb (fluffy white crystals from chloroform–petroleum hexane), m.p. 142–143°, was 0.87 g. (87%). The infrared spectrum of Vb included bands at 2.8, 8.0, 8.5, and 9.7 μ , but no band in the carbonyl region.

Anal. Calcd. for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 77.79; H, 5.40.

Oxidation of Vb.—A mixture of 0.07 g. of Vb, 0.05 g. of chromium trioxide, and 5 ml. of glacial acetic acid was warmed on a steam-bath for one hour; then the green solution was cooled and poured into water. The precipitate was washed and recrystallized from ethanol (with Norite treatment), yielding 0.035 g. (47%) of white crystals, m.p. 214.5–216.5°.

(14) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd. Ed., John Wiley and Sons, New York, N. Y., (1948), p. 171.

For comparison purposes, 1,8-di-*p*-anisoylnaphthalene was prepared by the method of Bachmann and Chu.¹² It melted at 217–218° (lit.¹² 215–216°). A mixture melting point determination and the infrared spectra showed that this compound was the same as that obtained by oxidation of Vb.

Attempted Benzoylation of Triphenylmethane with Stannic Chloride Catalyst.—A mixture of 1.80 g. of triphenylmethane, 20 ml. of benzoyl chloride, 2.0 ml. of stannic chloride and 30 ml. of carbon disulfide was refluxed for 15 hours and then hydrolyzed with dilute hydrochloric acid. The

carbon disulfide was removed by steam distillation and the organic residue taken up in ether. The ether solution was extracted with 5% sodium hydroxide to remove benzoic acid; then it was washed and dried. Removal of the ether and trituration with methanol gave 1.65 g. (92% recovery) of triphenylmethane, m.p. 91° (from methanol). No ketonic product could be detected by testing the ether solution of the neutral products with 2,4-dinitrophenylhydrazine reagent.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Course of Acid-catalyzed Rearrangement of Phenylcyclohexane Hydroperoxide and its Derivatives; Observations on the Properties and Oxidation of 6-Hydroxyhexanophenone

BY HAROLD KWART AND ROBERT T. KEEN^{1,2}

RECEIVED MAY 28, 1958

1-Phenylcyclohexyl hydroperoxide (I) rearranged almost quantitatively to cyclohexanone and phenol in acetic-sulfuric solution. The *p*-nitrobenzoate ester of this hydroperoxide gave an entirely analogous result under these conditions. When chromic anhydride-acetic acid solutions of the same acid strength were used to rearrange the hydroperoxide only *w*-benzoylvaleric acid was obtained. The latter reaction has been interpreted as proceeding *via* the chromate ester of the hydroperoxide followed by formation of a highly oxidizable keto-alcohol intermediate. The possible implications these results hold for the mechanism of acid-catalyzed rearrangement of analogous peroxy substances is also discussed. 6-Hydroxyhexanophenone and 1-phenyl-1,6-hexanediol have been synthesized and characterized. The remarkable ease with which these substances undergo chromic acid oxidation to the same product, *w*-benzoylvaleric acid, is considered as a clue to the mechanism of oxidative rearrangement of I.

The acid-catalyzed rearrangement of cumene (and related) hydroperoxides has been extensively investigated by several groups of workers.³ The similar acid-catalyzed rearrangement of decalyl perbenzoates and various *p*-substituted derivatives thereof have also been studied.⁴ The results in all cases are consistent with a mechanism involving concerted ionization of the oxygen-oxygen bond and bond formation at the developing cationic oxygen center.

The parallel to carbonium ion rearrangements has also been drawn^{3a,5} on the basis of migration aptitude data^{3c} and the correlation of rate with solvent polarity.^{4b,c} However, to extend this analogy to carbonium ion rearrangements it seemed desirable to demonstrate the preference for group migration. Such considerations have been well established for rearrangements like the Beckman,^{6a} the Pinacol,^{6b} the Schmidt^{6c} and Wagner-Meerwein,^{6d} to name a

few. For an examination of the course of migration during acid-catalyzed rearrangement 1-phenylcyclohexyl hydroperoxide (I) and various ester derivatives thereof were chosen as suitable models with which to demonstrate the relationship of an oxygen cation mechanism to ionic rearrangements involving electron deficient carbon and nitrogen.

Results and Discussion

A preparation of phenylcyclohexane hydroperoxide (I) containing a high concentration of the peroxide component has never been attained *via* the air oxidation of phenylcyclohexane.⁷ In our hands compound I, available commercially in a ca. 20% solution containing both hydrocarbon and alcohol impurity, could be readily concentrated to a useful product assaying at least 95.5% hydroperoxide. The successful method of preparation involved precipitation of the sodium salt⁸ and achieved complete separation of any detectable amounts of phenolic or ketonic contamination. It appears that the important point lies in the use of 50% sodium hydroxide since the more dilute base fails to give an easily isolated salt. Indeed, this latter observation was utilized in removing phenolic impurities by extraction with 5% sodium hydroxide.

When a sample of I prepared in this fashion was dissolved in an acetic-sulfuric acid solution and the resulting reaction was worked up after five minutes, the mixed product tested for the presence of both phenolic (Gibbs reagent) and ketonic components. The 2,4-dinitrophenylhydrazone of cyclohexanone could be recovered in nearly quantitative amounts

(7) Recently the characteristics of pure I were described for the first time by D. H. Hey, C. J. M. Sterling and C. H. Williams, *J. Chem. Soc.*, 1054 (1957), who prepared it by an entirely different method.

(8) Our results in this regard contrast strongly with reports in the recent literature; R. Foreman and H. Lankelma, *THIS JOURNAL*, **79**, 409 (1957); R. Criegee, *Ber.*, **77**, 22 (1944), and reference 4a.

(1) Part of this work is taken from the thesis of R. T. Keen submitted to the faculty of the University of Delaware in partial fulfillment of the degree of Master of Science in Chemistry, June 2, 1957.

(2) Presented before the 133rd Meeting of the American Chemical Society, April 14–19, 1958, San Francisco, Calif.

(3) (a) M. S. Kharasch, A. C. Poshkus, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 1458 (1951); (b) F. H. Seabold, Jr., and W. E. Vaughn, *THIS JOURNAL*, **75**, 3790 (1953); (c) P. D. Bartlett and J. D. Cotman, Jr., *ibid.*, **72**, 3095 (1950).

(4) (a) R. Criegee, *Ann.*, **560**, 127 (1948); R. Criegee and H. Dietrich, *ibid.*, **560**, 135 (1948); (b) P. D. Bartlett and J. L. Rice, *THIS JOURNAL*, **75**, 5591 (1953); (c) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(5) (a) J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949); (b) V. von E. Doering and L. Speers, *THIS JOURNAL*, **72**, 5515 (1950).

(6) (a) B. Jones, *Chem. Revs.*, **35**, 335 (1944); (b) P. I. Pollak and D. Y. Curtin, *THIS JOURNAL*, **72**, 961 (1950), *et seq.*; (c) P. A. S. Smith, *ibid.*, **70**, 3201 (1948); P. A. S. Smith and J. P. Horwitz, *ibid.*, **72**, 3718 (1950); C. L. Arcus, M. M. Combs and J. V. Evans, *J. Chem. Soc.*, 1498 (1956); (d) D. J. Cram, *THIS JOURNAL*, **71**, 3863, 3875, 3883 (1949); D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).