dium bisulfite. The mixture was extracted with five 50-ml. portions of benzene, and the water layer discarded. The benzene solution was extracted with 10% sodium bicarbonate, and the extracts acidified and extracted with benzene. The benzene solution was dried (sodium sulfate) and after removal of the solvent, distilled in a semi-micro column. There was no appreciable fore-run, and about 0.4–0.5 g. of phenylmethylacetic acid was obtained, b.p. 145–148° (15 mm.), n^{20}_D 1.5210, neut. equiv. 151.2 (calcd. 150.0). With S-benzylthiouronium chloride a flaky white salt, m.p. 151–152°, was obtained (mixed m.p. with an authentic sample, 151–152°). The yield of phenylmethylacetic acid was from 25–35% for the different alkylated phenols. Pertinent stereochemical data are given in Table I.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Stereochemistry of Aromatic Alkylations. II. The Thermal Rearrangement of Alkyl Aryl Ethers[1]

BY HAROLD HART AND HERBERT S. ELEUTERIO

RECEIVED JULY 13, 1953

The reaction of phenoxide ion with α-phenylethyl chloride is shown to be second order, and, since the α-phenylethyl phenyl ether formed from optically active halide had a high rotation, it is assumed that the reaction proceeded primarily with inversion (S_N2). The α-phenylethyl ethers of phenol, *p*-cresol, 2,6-xylenol and mesitol were prepared and their configurations thus assigned. α-Phenylethyl phenyl ether rearranged at 200° in five hours to give a 33% yield of α-phenylethylphenols (85% ortho). Similar results were obtained with the ethers of *p*-cresol and 2,6-xylenol, the latter giving 4-α-phenylethyl-2,6-dimethylphenol (23%). With optically active ethers, appreciable optical activity was retained, and the α-phenylethyl group migrated with retention of configuration, *even on para migration*. When optically active α-phenylethyl mesityl ether was treated with an excess of phenol at 200° for seven hours, a 44% yield of completely racemic α-phenylethylphenols was obtained. Thus, the reaction can apparently proceed in at least two manners: intramolecularly, with retention of configuration, and intermolecularly, *via* a symmetrical intermediate (radical or ion).

The rearrangement of an alkyl aryl ether to an alkylphenol can be thought of as an aromatic alkylation, and may take place as a true intramolecular rearrangement (as, for example, in the Claisen rearrangement of allyl phenyl ethers)[6] or intermolecularly *via* a variety of paths (involving ionic, radical, or molecular intermediates). We exclude from discussion here (but will consider in a later paper) rearrangements brought about by acidic catalysts such as zinc chloride or sulfuric acid,[2,3] and consider now only thermal transformations.

Alexander and Kluiber[4] have recently studied the thermal rearrangement of (–)α,γ-dimethylallyl phenyl ether and (–)α,β-dimethylallyl-2,6-xylyl ether, and found that both ortho and para rearrangement must have involved partial formation of the new carbon–carbon bond simultaneous with cleavage of the carbon–oxygen bond, because optical activity was retained. These results are compatible with the usual cyclic transition state considered to be operative in rearrangements of allyl phenyl ethers.[5,6] It should be noted, however, that the asymmetric center in the alkylated phenol is not the same as the one in the ether, but rather there is destruction of one asymmetric center and creation of another. We sought a case in which the asymmetric center in the ether and alkylated phenol would be the same (as in the secondary butyl phenyl ethers and phenols[2,3]).

Because the benzyl group is often similar in its behavior to the allyl group, there have been several attempts to carry out reactions analogous to the Claisen rearrangement with benzyl aryl ethers. Powell and Adams[7] were unable to isolate benzyl phenols from refluxed benzyl phenyl ether, but did obtain some toluene, possibly derived from benzyl radicals. Behagel and Freiensehner,[8] however, did isolate very low yields of benzyl- and dibenzylphenols, and also demonstrated cross-benzylation, as in the *p*-benzylation of methyl α-naphthyl ether by benzyl phenyl ether. When the reaction was carried out in quinoline[9] as the solvent, benzylquinolines and toluene were obtained in addition to benzylphenols, and Hickinbottom suggests cleavage into benzyl radicals.

We have prepared the optically active α-phenylethyl ethers of phenol, *p*-cresol, 2,6-xylenol and mesitol, and studied their thermal behavior. In order to establish the steric course of the reactions which occurred, it was necessary first to determine the stereochemical configurations of the ethers.

Kinetics and Stereochemistry of the Reaction of α-Phenylethyl Chloride with Phenoxide Ion.—The reaction of α-phenylethyl chloride with methoxide and ethoxide ions has been shown[10] to proceed primarily as a bimolecular nucleophilic displacement with inversion of configuration. Although it was felt that reaction with phenoxide ion would proceed in an analogous manner, kinetics were run to establish that this was in fact the case. The data for a typical run are given in Table I, and a

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[1] See footnote 1 of the preceding paper.

[2] See papers by M. M. Sprung and E. S. Wallis, THIS JOURNAL, **56**, 1715 (1934); W. I. Gilbert and E. S. Wallis, *J. Org. Chem.*, **5**, 184 (1940), on the stereochemistry of the catalyzed rearrangements.

[3] We are indebted to Dr. Patrick A. Diassi for an abstract of a paper by J. F. Lane and Diassi on the stereochemistry of the catalyzed rearrangement of *s*-butyl phenyl ether presented by them at a North Jersey Section Meeting-in-miniature early in 1952.

[4] E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951).

[5] D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

[6] J. P. Ryan and P. R. O'Connor, THIS JOURNAL, **74**, 5866 (1952); H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953).

[7] S. G. Powell and R. Adams, *ibid.*, **42**, 646 (1920).

[8] O. Behagel and H. Freiensehner, *Ber.*, **67B**, 1368 (1934).

[9] W. J. Hickinbottom, *Nature*, **143**, 520 (1939).

[10] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

summary for several different concentrations of phenoxide ion is shown in Table II. The small gradual decrease in the rate constants within a run (Table I) and also as the initial concentration of sodium phenoxide is increased (Table II) is in accord with what has been previously reported for similar reactions[11] and can be attributed to salt effects. Experiments which were run on a sufficiently large scale to permit product isolation showed that the major product was α-phenylethyl phenyl ether, with some nuclear alkylation also occurring.[12] Only traces of styrene were observed.

TABLE I

ALKYLATION OF PHENOXIDE ION BY α-PHENYLETHYL CHLORIDE IN ABSOLUTE ETHANOL AT 29.5 ± 0.1°

t (min.)	$a = 0.3500$ mole/l. of sodium phenoxide $a - x$	$b = 0.1667$ mole/l. of α-phenylethyl chloride $k_2 \times 10^3$ (l. mole^{-1} min.$^{-1}$)
795	0.3079	1.120
1291	.2899	1.093
2309	.2709	0.915
2554	.2666	0.906
4274	.2384	0.904

$k_2 = 2.303/t(a - b) \log [b(a - x)/a(b - x)]$

$k_{av} = 0.000988 \pm 0.000095$ l. mole^{-1} min.$^{-1}$

TABLE II

VARIATION OF k_2 WITH REACTANT RATIO

a (mole/l.)	a/b	$k_2 \times 10^3$
0.263	1.05	1.09 ± 0.10
.350	2.10	0.99 ± .09
.394	3.15	0.91 ± .04

When (+)α-phenylethyl chloride was refluxed with sodium phenoxide in absolute ethanol, (+)α-phenylethyl phenyl ether with a rather high degree of optical activity was obtained. The stereochemical results for this and other ether preparations are summarized in Table III. Since the ether formation presumably occurs with inversion of configuration, and since the configuration of α-phenylethyl chloride has been established, we tentatively assign the following configurations to the ethers in Table III.

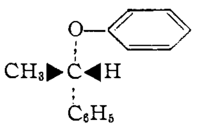
TABLE III

STEREOCHEMICAL RESULTS OF PREPARATION OF α-PHENYLETHYL ARYL ETHERS

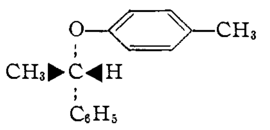
$C_6H_5CH(CH_3)—O—Ar$

Ar	Procedure[a]	Rotation of[b] α-phenylethyl chloride	Rotation of[b] the ether
Phenyl	A	30.4	11.34
	B	15.5	5.08
	C	7.02	2.30
p-Tolyl	A	26.5	4.06[c]
	C	22.9	3.75[d]
2,6-Xylyl	A	27.12	−12.57
Mesityl	A	22.9	−18.35

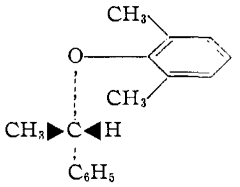
[a] Procedure A consisted in refluxing the chloride and phenol in acetone containing suspended potassium carbonate; procedure B, refluxing the chloride with sodium phenoxide in absolute alcohol; procedure C, refluxing the chloride with sodium phenoxide in benzene. [b] Rotations are $\alpha^{25}D$, homogeneous, $l = 1$ dm. [c] $[\alpha]^{25}D$, benzene, c 48.0. [d] $[\alpha]^{25}D$, benzene, c 40.0.



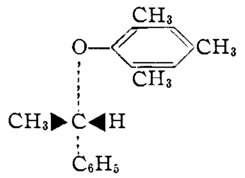
+41.1



+18.0



−51.0

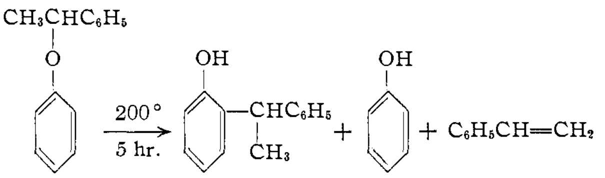


−88.0

The values for the rotations under each formula are minimum ones for the homogeneous liquid at 25°, $l = 1$ dm. except for the p-tolyl ether, where specific rotation in benzene, c 40 is given. These figures are based on the highest observed rotation ratio of ether to chloride, and use Burwell's experimental value for α-phenylethyl chloride.[13]

Because the stereochemistry of the preparation of α-phenylethyl phenyl ether is identical by all three procedures, and since inversion appears highly likely in procedure B, on which the kinetics were determined, we assume that in each case ether formation proceeds *via* nucleophilic displacement by phenoxide ions. Conductance measurements described in the experimental part lend support to this assumption. Although kinetics were run only with phenoxide ion, we assume the same mechanism to hold with the other three phenols studied. It is noted that a reversal in sign of rotation is attendant upon ortho methyl substitution in the aryl portion of the ether. Other ethers are now being prepared, and the effect systematically studied.

Thermal Rearrangement of α-Phenylethyl Aryl Ethers.—The most successful procedure for the thermal rearrangement of the ethers consisted in heating the ether without a solvent in an oil-bath at 200° for about five hours. Yields of alkylated phenols were 25–35%, and appreciable quantities of styrene and the non-α-phenylethylated phenols were also formed. With p-tolyl and 2,6-xylyl ethers, of course, only one α-phenylethylphenol was possible (the ortho and para isomers, respectively). But with the phenyl ether, where migration to the ortho and para positions was possible, spectrophotometric analysis[14] showed that the ortho isomer predominated (85%). The results for the phenyl ether are summarized in the equation



(85% o 15% p)

When the rearrangement was carried out with optically active ethers, the α-phenylethylphenols obtained were also optically active. A summary of the stereochemical experiments is given in Table IV.

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[11] O. R. Quayle and E. E. Royals, THIS JOURNAL, **64**, 226 (1942).

[12] H. Hart and H. S. Eleuterio, *ibid.*, **76**, 516 (1954).

[13] See footnote 16 of ref. 12.

[14] H. Hart, *Anal. Chem.*, **24**, 1500 (1952).

TABLE IV

THERMAL REARRANGEMENT OF OPTICALLY ACTIVE α-PHENYLETHYL ARYL ETHERS

Ar	Rotation of the ether[a]	Rotation of the alkylated phenol[a]
Phenyl	5.08	−0.82[b]
p-Tolyl	4.06[c]	− .74
2,6-Xylyl	−12.57	.40

[a] α^{25}_D, homogeneous, l = 1 dm. [b] 85% *o*, 15% *p*. [c] $[\alpha]^{25}_D$, benzene, c 48.0.

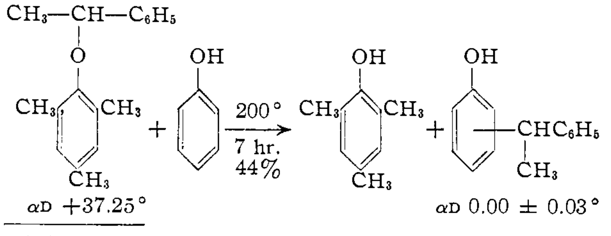
The configurations and minimum rotations of the alkylated phenols formed during this rearrangement were assigned in the preceding paper.[12] It therefore is possible to describe the stereochemistry of the rearrangement, including an estimate of the maximum % racemization accompanying the process.

In each case, whether the migrating group entered the ortho or para positions, the rearrangement proceeded with retention of optical configuration. Whether the rearrangement was ortho or para, the extent of retention of optical purity was about the same, approximately 20%.[15] This is a minimum value.

We propose that the rearrangement is at least in part truly intramolecular, because a portion of the α-phenylethyl groups migrate without loss of stereochemical configuration. In this manner, the reaction may be considered analogous to certain other intramolecular aromatic rearrangements.[16]

The formation of cleavage products, as well as the fact that the α-phenylethylated phenols are not formed with 100% retention of optical purity, indicates that the reaction also proceeds simultaneously by an alternate, intermolecular route. We favor an ionic, rather than a radical path, because no ethylbenzene was isolated (although it may well be that the α-phenylethyl radical loses a hydrogen atom more readily than it abstracts one). Loss of optical purity may be due to the formation of a symmetrical α-phenylethyl intermediate (ion or radical) which either loses hydrogen to form styrene, or reacts with the phenol to form racemic alkylate. Alternatively, loss of optical purity may be due to bimolecular alkylation of the phenol by the original ether, with resulting inversion of configuration.

In order to decide between these two alternatives, the α-phenylethyl ether of mesitol was prepared, and heated in an excess of phenol for seven hours at 200°. From optically active ether, a 44% yield of completely racemic α-phenylethylphenols was obtained.



We conclude that a bimolecular nuclear alkylation with inversion does not occur.[17] This experiment also offers further support for the intramolecularity of part of the reaction when an ortho or para position is available, because when the path is necessarily intermolecular, all optical activity is lost.

Experimental

Sodium Phenoxide and α-Phenylethyl Chloride. Kinetic Procedure.—Solutions of sodium phenoxide (0.525 *M*) and α-phenylethyl chloride (0.500 *M*) in absolute ethanol were mixed and maintained at 29.5 ± 0.1°. At various time intervals, 5-ml. aliquots were withdrawn and transferred to 100 ml. of 50% aqueous ethanol; unreacted base was immediately determined by titration with 0.09948 *N* hydrochloric acid to a lacmoid indicator end-point.

Product Isolation.—A solution of 250 ml. of 0.525 *M* sodium phenoxide and 250 ml. of 0.500 *M* α-phenylethyl chloride in absolute ethanol was kept at 29.5° for 24 hours. The mixture was diluted with water and extracted with petroleum ether. The water layer was discarded, and the petroleum ether solution extracted with 10% aqueous sodium hydroxide, water and then dried over anhydrous sodium sulfate. After removal of the solvent, there was recovered 12.0 g. of unreacted α-phenylethyl chloride and 2.5 g. of α-phenylethyl phenyl ether, b.p. 143–145° (10 ml.). Acidification of the alkaline extracts, extraction of the liberated oil with benzene, and subsequent drying and distillation gave 7.5 g. of phenol and 1.0 g. of a mixture of *o*- and *p*-α-phenylethylphenols.

Preparation of α-Phenylethyl Aryl Ethers.—Three procedures for preparing the ethers were reported in the experimental part of the previous paper.[12] The procedure using acetone, potassium carbonate, α-phenylethyl chloride and the particular phenol, with reflux times as indicated previously, was the most successful. Since the ethers have not been previously described, their analyses and physical properties are given in Table V. Although the carbon–hydrogen analyses are not highly diagnostic, it is felt that the structures are as assigned, from the method of synthesis, from the thermal rearrangement products of the ethers, and from the products of cleavage by hydrogen chloride.[18] The stereochemistry of the ether preparations is summarized in Table III.

TABLE V

ANALYSES AND PROPERTIES OF SOME α-PHENYLETHYL ARYL ETHERS. C_6H_5—CH(CH_3)—O—Ar

Ar	M.p. or b.p., °C.	Analyses, % Carbon Calcd.		Hydrogen Calcd.	
		Calcd.	Found	Calcd.	Found
C_6H_5	38–39	84.9	85.2	7.1	7.3
p-CH_3-C_6H_4	49–50	84.9	85.0	7.6	7.8
2,6-$(CH_3)_2$-C_6H_3	31–32	84.9	85.1	8.0	8.1
2,4,6-$(CH_3)_3$-C_6H_2	142 (4 mm.)	85.0	85.1	8.4	8.5

Conductance Measurements.[19]—A solution of 0.1 mole of phenol in 50 ml. of acetone, in a conductance cell, had a resistance of 51,000 ohms. In the same cell, the filtrate from a suspension of 0.1 mole of potassium carbonate in 50 ml. of acetone had a resistance > 100,000 ohms, but the filtrate from a suspension of 0.1 mole of potassium carbonate in a solution of 50 ml. of acetone containing 0.1 mole of phenol, had a resistance of only 39 ohms. This we take as evidence for the presence of ions, presumably phenoxide, in the solution. The stereochemistry of ether preparation (Table III) by the acetone–potassium carbonate procedure was the same as by the phenoxide ion–ethanol procedure.

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(15) The calculation for the 2,6-xylyl ether is 51.0 × 0.40 × 100/12.57 × 8.6 = 18.9% retention of optical purity.

(16) See, for example, C. K. Ingold "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XI.

(17) One of the referees has suggested that racemization may be the result of transetherification reactions. This possibility is not excluded by the present experiments, although the *complete* loss of activity in the methyl ether case does not favor this interpretation.

(18) Reported in preliminary fashion at Atlantic City, Sept., 1952, Abstracts p. 3M. The stereochemistry and kinetics of the cleavage of these ethers by hydrogen halides has been investigated, and will be reported in a separate paper (work with H. S. Eleuterio and R. Elia)

(19) We are grateful to Bradford H. Thompson for these measurements.

General Procedure for the Thermal Rearrangement of α-Phenylethyl Aryl Ethers.—Twelve grams of the ether was placed in a modified Claisen flask, and immersed in an oil-bath at 200° for five hours. During this time, a small amount of styrene distilled from the flask (dibromide m.p. 73°). The reaction mixture was cooled, taken up in petroleum ether, and extracted with 10% aqueous sodium hydroxide until a small portion of the alkaline extract gave only a slight opalescence on acidification. The alkali insoluble material was dried over anhydrous sodium sulfate, the solvent removed, and the residue distilled. In each case, no ether was recovered, but an unidentified high-boiling (180–240° (10 mm.)) material was obtained (1–2 g.).

The alkaline extracts were combined, acidified with hydrochloric acid, and the resulting oil taken up in benzene, dried, solvent removed by distillation and the residue distilled under reduced pressure. In each case, some of the phenol from which the ether had been prepared, and some α-phenylethylated phenols were obtained. The yields of materials are summarized in Table VI. The stereochemical results of the thermal rearrangements were given in Table IV.

TABLE VI

THERMAL REARRANGEMENTS OF α-PHENYLETHYL ARYL ETHERS

Ar	Starting ether G.	Starting ether Moles	Recovered ArOH G.	Recovered ArOH Moles	α-Phenylethylated ArOH G.	α-Phenylethylated ArOH Moles
C_6H_5	12.0	0.060	1.5	0.016	4.0	0.020
p-CH_3–C_6H_4	12.0	.056	2.0	.018	3.0	.014
2,6-$(CH_3)_2$–C_6H_3	12.0	.053	3.0	.025	2.7	.012

α-Phenylethyl Mesityl Ether and Phenol.—A mixture of 8 g. (0.033 mole) of α-phenylethyl mesityl ether (α_D +37.25°) and 14 g. (0.15 mole) of phenol was heated in an oil-bath at 200° for 7 hours. The reaction mixture was worked up as described in the general procedure for the thermal rearrangements. No alkali insoluble material was obtained. Distillation of the alkali-soluble fraction gave 12.0 g. of a mixture of phenol and mesitol, and 3.0 g. of α-phenylethylphenols (72% ortho), b.p. 160–170° (5 mm.), α_D 0.00 ± 0.03°.

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[CONTRIBUTION OF THE LEWIS FLIGHT PROPULSION LABORATORY, NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Dicyclic Hydrocarbons. VII. Synthesis and Physical Properties of Some 1,3-Diphenyl- and 1,3-Dicyclohexyl-2-alkylpropane Hydrocarbons[1]

BY ROBERT M. CAVES, R. L. MCLAUGHLIN AND P. H. WISE

RECEIVED JULY 13, 1953

The methyl, ethyl and propyl homologs of 1,3-diphenyl- and 1,3-dicyclohexyl-2-alkylpropane were synthesized from 1,3-diphenyl-2-alkyl-2-propanols, which were prepared by the reaction of benzylmagnesium chloride with acid halide or esters. Dehydration of the alcohols with subsequent hydrogenation of the olefins was the method used to obtain the ethyl and propyl aromatic hydrocarbons, whereas the methyl hydrocarbon was obtained by the direct hydrogenolysis of the alcohol. The dicyclohexyl hydrocarbons were obtained by complete hydrogenation of the aromatic olefins or hydrocarbons. The physical properties obtained were melting point, boiling point, density, refractive index, heat of combustion and kinematic viscosity. Two new compounds, 1,3-diphenyl- and 1,3-dicyclohexyl-2-propylpropane, are reported.

Introduction

The methyl, ethyl and propyl homologs of the 1,3-diphenyl- and 1,3-dicyclohexyl-2-alkylpropane series were among those hydrocarbons of interest at this Laboratory for an investigation of the effects of structure on combustion characteristics and physical properties.[2] Although the methyl and ethyl hydrocarbons of both series have previously been described,[3,4] the absence of some physical properties and lack of agreement among some of the published properties necessitated the work described herein. (References 3 and 4 give with each physical constant listed comprehensive primary references which cover adequately the various methods of syntheses for these hydrocarbons.)

The general method used for obtaining the hydrocarbons started with the reaction of two moles of benzylmagnesium chloride with one mole of either an ester[5] or a halide of an aliphatic acid to produce the 1,3-diphenyl-2-alkyl-2-propanols. The ethyl- and propylcarbinols were dehydrated to the olefins from which the aromatic hydrocarbons were obtained by hydrogenation of the double bond. The methyl aromatic hydrocarbon on the other hand was obtained in good yield directly from the methylcarbinol by hydrogenolysis. However, when this reaction was tried with the ethyl- and propylcarbinols, it failed to give satisfactory products and yields. The 1,3-dicyclohexyl-2-alkylpropanes were obtained by complete hydrogenation of either the purified aromatic hydrocarbons or intermediate olefins.

The syntheses were carried out on a scale to provide 500 ml. of each hydrocarbon with an estimated purity of about 99 mole per cent. It was possible to calculate the purity from the time–temperature melting curve only in the case of 1,3-dicyclohexyl-2-methylpropane. The time–temperature melting curve obtained for 1,3-diphenyl-2-methylpropane was too short for a valid estimation of purity. Since none of the other four compounds could be induced to crystallize, it can only be stated that the purities of these five hydrocarbons are believed to be of the same order as that of 1,3-dicyclohexyl-2-methylpropane, inasmuch as all the compounds were prepared and purified by similar methods.

In Table I, the physical properties and carbon–hydrogen analyses of the six 1,3-diphenyl- and 1,3-dicyclohexyl-2-alkylpropanes are presented. The apparatus and procedure used in the determination

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(1) Presented before the Organic Division of the American Chemical Society, Buffalo, N. Y., March 24, 1952.

(2) Previous papers of this series giving physical properties of hydrocarbons closely related to these hydrocarbons are: K. T. Serijan and P. H. Wise, THIS JOURNAL, **74**, 365 (1952); P. H. Wise, K. T. Serijan, and I. A. Goodman, National Advisory Committee Aeronautical Report 1003 (1951).

(3) G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, pp. 210–211.

(4) G. Egloff, *ibid.*, Vol. III, 1946, pp. 360 and 370.

(5) M. Tiffeneau and J. Levy, *Bull. Soc. Chim.*, **33**, 735 (1923)