chromatography showed the camphene to be at least 96% pure.

Pyrolysis of cyclohexylcarbinyl borate. A mixture of cyclohexylcarbinol (5 g.) and boric acid (2.7 g.) was heated slowly to 140°, and the water which distilled was separated. The bath temperature was then raised to 290°. At this temperature the olefinic product began to distill. The yield of olefinic product was 3.8 g. (91%). Analysis of the olefin mixture by vapor phase chromatography on a two meter Perkin-Elmer R column at 100° gave the results shown below. The two analyses are based on separate experiments and are not duplicate analyses of the same mixture. The olefins were separated by preparative scale vapor phase chromatography and identified by comparison of infrared spectra with the spectra of authentic samples.[6]

Run/Product	VIII	IX	X
1	5.9	82.3	11.8
2	6.1	81.9	12.0
Average	6.0	82.1	11.9

Oxalic acid dehydration of cyclohexylcarbinol. A mixture of cyclohexylcarbinol (5 g.) and oxalic acid (30 g.) was slowly heated to 135°. At this temperature water and olefinic product distilled. The yield of olefinic product (after drying) was 3.9 g. (92%). This mixture (analyzed as above) contained methylenecyclohexane (10.2%), 1-methylcyclohexene (82.2%) and cycloheptene (7.6%).

Pyrolysis of cyclobutylcarbinyl borate. A mixture of cyclobutylcarbinol (0.8 g.) and boric acid (0.58 g.) was slowly heated to 140° and maintained at this temperature until water no longer distilled. The bath temperature was then slowly raised to 245–255°. At this temperature the olefinic product distilled smoothly. The product was shown to be a single olefin by vapor phase chromatography (Perkin-Elmer R column, 34°). The infrared spectrum of the product was identical to that of authentic cyclopentene.

Formation and hydrolysis of cyclohexylcarbinyl borate. A mixture of cyclohexylcarbinol (5 g.) and boric acid (2.7 g.) was slowly heated to 140°, and the water which distilled was separated. The bath temperature was then raised to 290° and maintained at this temperature for 10 min. The mixture was cooled and 100 ml. of methanol and 3 ml. of water were added. This solution was refluxed on the steam bath for 3 hr., and the methanol was removed. The residue was dissolved in ether and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave unchanged cyclohexylcarbinol identical in infrared absorption with an authentic sample.

Formation and hydrolysis of 3,3-dimethyl-2-butyl borate. A mixture of 3,3-dimethyl-2-butanol (10 g.) and boric acid (6 g.) was heated slowly to 120°, and the water which distilled was separated. The bath temperature was then raised to 250° and maintained for 10 min. at this temperature. After cooling, the borate was dissolved in 100 ml. of methanol and 3 ml. of water. This solution was refluxed for 1 hr., and the methanol was removed. The residue was taken up in ether and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave unchanged 3,3-dimethyl-2-butanol identical in infrared absorption to the starting alcohol.

Acknowledgment. The authors acknowledge their indebtedness to Professor C. H. De Puy for many lively discussions of ester pyrolysis.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOYOLA UNIVERSITY]

Ring Size Effects in the Neophyl Rearrangement. II. The Decarbonylation of (1-Methylindanyl)acetaldehyde[1,2]

JAMES W. WILT AND CHARLES A. SCHNEIDER

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(1-Methylindanyl)acetaldehyde (IV) has been prepared and characterized. Its decarbonylation under free radical conditions led to 1,1-dimethylindane (V) and 2-methyltetralin (VI) in good yield. The 35% rearrangement found is significantly less than that observed in the parent system of β-phenylisovaleraldehyde. The decrease in rearrangement percentage is attributed to the planar, fixed attitude of the molecule which retards attainment of the Ar_1-3 type transition state. The existence of a bridged radical as a reaction intermediate in this reaction has been rendered unlikely by a kinetic investigation. The effect of excess peroxide on the rearrangement was also investigated.

The rearrangement exhibited by neophylaldehydes during homolytic decarbonylation has been attributed primarily to steric effects.[2] In an earlier study from this laboratory,[2] two compounds, albeit sterically similar, gave appreciably different rearrangement percentages in this reaction. It was felt that these two substances, (1-phenylcyclopentyl)-acetaldehyde and (1-phenylcyclohexyl)acetaldehyde, differed in their abilities to achieve the requisite transition state for rearrangement because of hindered rotation of the phenyl group in the cyclopentyl analog. Molecular models indicated interference of the *ortho* hydrogens of the aromatic ring by an adjacent cyclopentyl ring hydrogen.[3]

To lend support to the earlier contention as well as to learn more of the steric requirement for rearrangement in neophyl systems, a study was needed of a model compound which would have the

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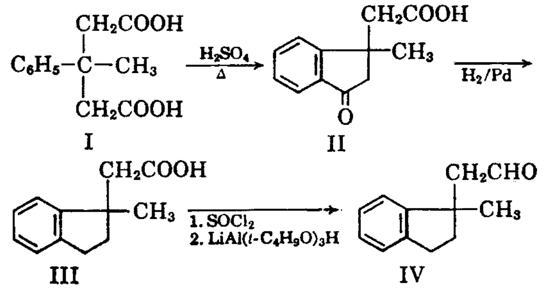
[1] (1) This report is taken from the M. S. thesis of C. A. S., Loyola University, February 1961.

[2] (2) For Paper I and references, see J. W. Wilt and Bro. H. Philip, F. S. C., *J. Org. Chem.*, 25, 891 (1960).

[3] (3) An additional reason for the different rearrangement abilities of the 1-phenylcyclohexyl- and 1-phenylcyclopentylcarbinyl radicals studied earlier[2] might be the relief of the axial strain of the carbinyl group and hydrogens 1,3- to it in the former. We thank Profs. W. H. Urry and N. C. Yang of the Department of Chemistry of the University of Chicago for this suggestion.

rotation of the aromatic ring more seriously restricted than was the case earlier. Such restricted rotation should reflect itself in a still further decreased extent of rearrangement relative to the aforementioned compounds and some standard system. As before,[2] the parent neophyl radical derived from β-phenylisovaleraldehyde was chosen as the standard.

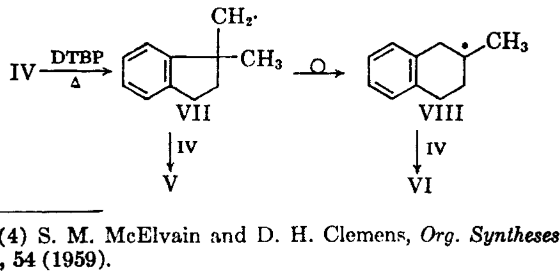
The model substance chosen was (1-methylindanyl) acetaldehyde (IV), the synthesis of which is shown below. β-Phenyl-β-methylglutaric acid (I)[4]

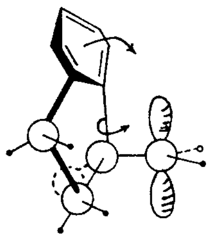


was cyclized by means of concentrated sulfuric acid to the acid (II). Catalytic reduction of this keto acid gave III, which was converted *via* the acid chloride to the aldehyde (IV) by the method of Brown and Subba Rao.[5] The yields throughout were good.

In addition to the obviously restricted rotation of the aromatic ring, IV seemed an appropriate model compound for this study for two additional reasons; namely, that whatever electronic effects exist in this rearrangement might be expected to be about equal for IV and the structurally similar β-phenylisovaleraldehyde, and the two systems are alike in that the steric compression due to the quaternary carbon is relieved by rearrangement.

IV yielded 1,1-dimethylindane (V) and 2-methyltetralin (VI) in 76% yield upon decarbonylation with 10 mole percent of di-*t*-butyl peroxide at 160° (bath). The percentage of rearranged hydrocarbon (VI) in the product was 34.5 ± 0.3% from several experiments, a significant decrease from the 57 ± 3% rearrangement reported[6] for β-phenylisovaleraldehyde. This decrease might conceivably be due to: (a) more dimer (or other type) products which lessen the yield of V and VI; (b) an increased chain transfer ability of IV; or (c) an increased barrier to rearrangement in the radical VII. Points (a) and (b) may be answered from the yield of V and VI, the amount of peroxide needed to decarbonylate IV, and the time needed to achieve essentially complete reaction. The data (see Experimental) for IV are very similar to that reported[6] for β-phenylisovaleraldehyde and indicate that the two aldehydes do not differ significantly in these regards. With reference to (c), the drawing below of the radical VII illustrates the difficulty which arises when an Ar₁-3[7] type transition state is demanded for this neophyl rearrangement. The arrows indicate the movements required of the aromatic moiety to achieve this transition state. This state would





VII

be manifestly of high energy because of the torsional strain on the planar five-membered ring.[8] The fact that rearrangement does occur, but some 22% decreased from the parent system, indicates either that the Ar₁-3 state is achieved at the expense of added strain caused by the geometry of the molecule, but slower than with neophyl, or, that a compromise is effected. This compromise would involve only slight torsional strain in the five-membered ring but with less than the maximum overlap between the engaging orbitals demanded by the Ar₁-3 state. In either case the result seems clear: when the aromatic ring in a neophyl system is hindered in its rotation to achieve the spiro character of the (heretofore assumed) transition state, rearrangement decreases. The earlier conclusions[2] thus are supported.[9]

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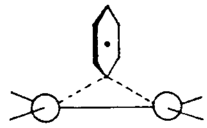
[4] S. M. McElvain and D. H. Clemens, *Org. Syntheses*, **39**, 54 (1959).

[5] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

[6] F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **75**, 2532 (1953).

[7] This is a convenient notation for neighboring group assistance by β-aromatic groups. See S. Winstein, *Chem. & Ind.*. 562 (1954); S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); and R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957). The geometry for this transition state is drawn below to emphasize the right angle relationship of the rings involved.



[8] For a study bearing on the coplanarity of the two rings in indane derivatives, see R. Huisgen, W. Rapp, I. Ugi, and H. Walz, and E. Mergenthaler, *Ann.*, **586**, 1 (1954).

[9] A study of a neophyl type radical which cannot achieve *any* overlap of the type described above is under way in order to test the strictness of the geometric requirement in this rearrangement.

As an additional part of this study, a product analysis of the reaction at various times was performed. The results are given in Table I. The value of this kinetic study lies in the clear demonstration that the rate of rearrangement increases with time relative to the rate of formation of the nonrearranged product. The evidence indicates that the two hydrocarbons produced result from two different radicals. The possibility that a single bridged radical could be the direct intermediate for both the products is therefore highly unlikely. The same conclusion has been drawn for the neophyl rearrangement by a number of workers.[2]

TABLE I

DECARBONYLATION OF (1-METHYLINDANYL)ACETALDEHYDE (IV)[a]

Time, Min.	Product Composition[b] DMI[c]	MT[d]
5	100	0
15	88	12
30	80	20
60	77	23
180	70	30
400	65	35

[a] at 160° (bath). For concentrations, etc., see decarbonylation studies, experiment 4 (Experimental). [b] Percentage composition by vapor phase chromatography. [c] 1,1-Dimethylindane. [d] 2-Methyltetralin.

Lastly, the previously unreported effect of a large initial initiator concentration on the neophyl rearrangement was investigated. When IV was decarbonylated using a 6:1 mole ratio of di-*t*-butyl peroxide to IV, the rearrangement percentage rose to 46%. Slighter increases in initiator were essentially without effect, however. The action of the large increase in peroxide is felt to be the result of a dilution effect on IV, since dilution of the aldehyde increases rearrangement.[2]

Recently the isomerization of quaternary alkylbenzenes by di-*t*-butyl peroxide has been reported.[10] Since our results are valid only if no isomerization of V to VI occurred, such an isomerization under the conditions of these decarbonylations was investigated and found to be absent.

EXPERIMENTAL

Melting points were determined on a calibrated Fisher-Johns melting point block. Boiling points are not corrected for stem exposure. Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 21 instrument, using neat liquids and solids in potassium bromide pellets. A Perkin-Elmer Model 154 Fractometer was employed for the vapor phase chromatographic work.

β-Phenyl-β-methylglutaric acid (I). The acid was prepared as reported,[4] m.p. 136–140° (76%), lit. m.p. 136–139°. The C=O absorption was at 5.83 μ.

(1-Methyl-3-oxoindanyl)acetic acid (II). I (20 g., 0.09 mole) and concentrated sulfuric acid (150 g.) were heated with stirring at 100° for 17 hr. The hot mixture was poured over ice and the precipitated acid collected and washed with water. The air-dried solid was recrystallized from methanol-water to give II as a colorless solid (13.1 g., 70%, m.p. 125°). The C=O absorptions were at 5.76 μ (acid) and 5.95 μ (ketone).

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; neut. equiv. 204. Found: C, 70.45; H, 6.02; neut. equiv., 204.

The oxime of II was prepared in standard fashion, m.p. 159–160°.

Anal. Calcd. for $C_{12}H_{13}NO$: N, 6.39. Found: N, 6.33.

(1-Methylindanyl)acetic acid (III). Both the Clemmensen and Huang-Minlon reductions failed to give good yields of III (17 and <5%, respectively). Catalytic hydrogenolysis worked well, however. II (30 g., 0.15 mole) in ethanol (95%, 120 ml.), containing sulfuric acid[11] (1 g.) was hydrogenolyzed at 40 p.s.i. using palladium-on-charcoal (10%, 1 g.). The hydrogen uptake was theoretical. The catalyst was filtered off and the solution diluted with water (120 ml.). Sodium hydroxide (12 g.) was then added and the ethanol was removed by distillation. The basic, aqueous solution was chilled to 10° and III was precipitated by the addition of excess, dilute (10%) hydrochloric acid. After refrigeration overnight, the precipitate was collected and recrystallized from methanol-water to give crystalline III as a white solid (23.6 g., 83%, m.p. 57–58°). The C=O absorption was at 5.86 μ.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42; neut. equiv., 190. Found: C, 75.94; H, 7.49; neut. equiv., 193.

The *S*-benzylisothiuronium salt was readily prepared, m.p. 125°.

Anal. Calcd. for $C_{20}H_{24}N_2SO_2$: C, 67.38; H, 6.79. Found: C, 67.57; H, 6.72.

(1-Methylindanyl)acetaldehyde (IV). The acid chloride of III was prepared using thionyl chloride in the usual fashion (85–90%, b.p. 100° at 1.5 mm.). The compound was used directly in the following reduction, following closely the method of Brown and Subba Rao.[5] From the acid chloride (34.3 g., 0.165 mole) and lithium tri-*t*-butoxyaluminohydride (42 g., 0.165 mole) in bis-2-ethoxyethyl ether, using the literature technique, the aldehyde was obtained as a colorless oil (10.7 g., b.p. 130° at 10 mm., n_D^{20} 1.5318, d_4^{20} 1.029). The aldehyde C—H absorption was at 3.46 μ and the C=O absorption at 5.73 μ.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.59; H, 8.20.

The 2,4-dinitrophenylhydrazone was easily prepared, m.p. 153.5°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.77.

The semicarbazone, m.p. 113°, afforded further characterization.

Anal. Calcd. for $C_{13}H_{17}N_3O$: N, 18.17. Found: N, 18.07.

From basic extracts of the reaction mother liquor, III was recovered (14.7 g.). The yield of aldehyde was therefore 86.5%. Air oxidation of exposed IV led to the acid III in quantitative yield in 5 days. IV could be kept in sealed ampoules under nitrogen with no change in the infrared spectrum, although a pale yellow color developed.

Preparation of reference hydrocarbons. 1,1-dimethylindane (V). This hydrocarbon was prepared by the catalytic hydrogenolysis (40 p.s.i.) of 3,3-dimethylindanone-1[12] (8.0 g., 0.05 mole) in methanol (30 ml.) containing sulfuric acid (1.25 g.) using palladium-on-charcoal (10%, 1.25 g.). Filtration of the reaction material, neutralization with sodium carbonate solution (10%) and extraction with ether followed. The hydrocarbon was obtained by distillation through a Piros-Glover spinning band column (7 g., 96%, b.p. 40° at 0.9

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[10] H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2921 (1960).

[11] The sulfuric acid dramatically hastened the reaction. Others have noted this same effect—*e.g.*, K. Kindler, E. Schärfe, and P. Henrich, *Ann.*, **565**, 51 (1949).

[12] C. F. Koelsch and C. D. Le Claire, *J. Org. Chem.*, **6**, 516 (1941).

mm., n_D^{20} 1.5139, d_4^{20} 0.919, lit. b.p. 191° (atm.),[13] n_D^{20} 1.5141[14]). The infrared spectrum of V was consistent with its structure and possessed the doublet at 7.27 μ and 7.38 μ due to the *gem*-dimethyl grouping. V was free of contaminants in vapor phase chromatography (retention time of 7 min., 160°, Perkin-Elmer silicone oil column "O").

2-Methyltetralin (VI). Tetralone-1 (14.6 g., 0.1 mole) was converted[15] to its 2-hydroxymethylene derivative[16] (14.6 g., 84%, b.p. 147° at 4 mm., n_D^{20} 1.6339, lit.[16] b.p. 105–107° at 1 mm., n_D^{19} 1.6341). This derivative (12.3 g., 0.071 mole) was then alkylated with methyl iodide (20.2 g., 0.124 mole), using the technique reported for the 6-methoxy analog,[17] which employs sodium amide in dimethylformamide as the base, to give 2-methyltetralone-1 (4.3 g., 39%, b.p. 115° at 10 mm., n_D^{20} 1.5544, 2,4-dinitrophenylhydrazone m.p. 224°, lit.[18] b.p. 126° at 12.5 mm., n_D^{20} 1.5541, 2,4-dinitrophenylhydrazone m.p. 224°). Catalytic hydrogenolysis (40 p.s.i.) of this ketone (3.6 g., 0.023 mole) in methanol (20 ml.) and sulfuric acid (0.25 g.) over palladium-on-carbon (10%, 0.25 g.), as described for V above, led to VI (2.2 g., 67%, b.p. 222° (atm.), n_D^{20} 1.5261, lit.[18] b.p. 219.8° at 751 mm., n_D^{20} 1.5267, d_4^{20} 0.9432). The infrared spectrum of VI was consistent with its structure. VI possessed at 160° retention times of 12.5 min. ("O" column above) and 24 min. (Perkin-Elmer didecyl phthalate "A" column). A trace contaminant (< 0.5%) was neglected in the subsequent use of VI.

Decarbonylation studies. The technique employed was that used earlier,[2] except that no distillation of the reaction material was performed. Rather, when gas evolution ceased or at various known times, measured aliquots of the material were withdrawn through a small side neck of the flask capped with a rubber septum and analyzed by vapor phase chromatography for V and VI through comparison with standards. The ratio of areas method was used. The following are, for each *experiment*, the mmoles of IV, mmoles of di-*t*-butyl peroxide, total reaction time (min.), carbon monoxide evolved (%), and *rearrangement* (%): *1*, 14, 3.1, 400, 89, *35; 2*, 11.5, 23, 495, 89, *33; 3*, 13.7, 82, 360, 89, *46; 4*, 9.9, 2, 400, 81, *35; 5*, 9.5, 0.95, 395, not determined, *34*. The bath temperature for all experiments was 160° and the yield of V and VI was 76% in experiment 4 and 81% in experiment 3. The di-*t*-butyl peroxide was 10 mole percent initially in experiments 1 and 4, with the additional amount being added at 340 and 120 min., respectively.

Attempted isomerization of V. V (0.25 g., 1.71 mmoles) and di-*t*-butyl peroxide (0.025 g., 0.17 mmole) were heated at 160° (bath) for 8 hr., the time of the longest decarbonylation study. Analysis by vapor phase chromatography showed but a trace of product other than V. Likewise, a completed decarbonylation reaction residue (65% V, 35% VI) was again heated under the above conditions with a small quantity of added di-*t*-butyl peroxide and IV for 100 min. The ratio of V and VI at the end of this time was unchanged (vapor phase chromatography).

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(16) E. Ott and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 6266 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

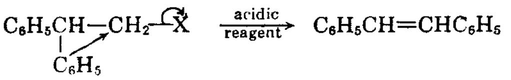
Unrearranged Elimination and Substitution Products from 2,2-Diphenylethyl Tosylate with Bases. Rearrangement with Acidic Reagents[1]

PHILLIP J. HAMRICK, JR.,[2] AND CHARLES R. HAUSER

Received May 5, 1961

2,2-Diphenylethyl tosylate underwent rearrangement with acidic reagents to form stilbene, but produced unrearranged elimination and/or substitution products with basic reagents. The reactions with alkali amides in liquid ammonia and with alkali methoxides in refluxing methanol gave exclusively 1,1-diphenylethylene, whereas those with piperidine and morpholine yielded largely the corresponding tertiary amines. Certain other basic reagents produced both elimination and substitution products.

Acidic reagents effect the elimination of HX from alcohol (I) and its tosylate or halide (II) accompanied by rearrangement to form stilbene. Presumably these reagents coordinate with a free pair of electrons on X to promote its ionization and the shift of a phenyl group (Equation 1).



$$\underset{\displaystyle C_6H_5}{C_6H_5\overset{|}{C}H}-CH_2-X \xrightarrow[\text{reagent}]{\text{acidic}} C_6H_5CH{=}CHC_6H_5 \qquad (1)$$

I. X = OH
II. X = OTs, Cl, or Br

Earlier workers have obtained stilbene from alcohol (I) on dehydration with phosphorus pentoxide in refluxing benzene,[3,4] and from tosylate (II) on heating in glacial acetic acid.[5] A kinetic study of the latter reaction afforded evidence for participation of the phenyl group in the ionization of X and the rearrangement.[5]

We have isolated stilbene in high yields on treatment of alcohol I with hydrogen bromide or phos-

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[1] Supported by the National Science Foundation.

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