weight of the crude product was 22 g. By adding petroleum ether to the hydrocarbon portion of the filtrate, additional solid product could be obtained to slightly increase the yield.

The *o*-benzoylbenzoic acid was recrystallized by dissolving it in a small volume of hot toluene and then adding just enough petroleum ether to cause precipitation as the solution cooled. The yield of purified acid obtained in this way was 16.8 g., m.p. 128.8–129.8°. The product was further recrystallized to constant melting point.

Neutralization Equivalents.—The neutralization equivalent for each acid was determined by dissolving a 50- to 80-mg. sample in 50 ml. of 95% ethyl alcohol. The solution was titrated with aqueous sodium hydroxide (approx. 0.03 *N*) using phenolphthalein as the indicator. Previous to the titration a blank was determined for the alcohol.

Melting Point Determinations.—The melting ranges given in Tables I and II were taken from the point where the compound first wetted the side of the capillary tube to the point where only a clear liquid was observed. The rate of temperature rise near the melting point was a maximum of $^1/_2$° per minute. The values were determined by the use of calibrated Anschütz precision thermometers of the total immersion type. The melting point apparatus was similar to that described by Merriam.[20]

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(20) F. Merriam, *Anal. Chem.*, **20**, 1245 (1948).

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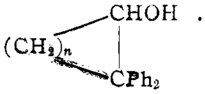
Molecular Rearrangements. III. The Retropinacolone Rearrangement of 2,2-Diphenylcycloalkanols[1]

BY ROBERT E. LYLE, NATHAN B. MARTIN, JR.,[2] AND HERBERT L. FIELDING[2]

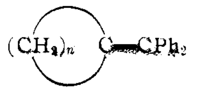
RECEIVED APRIL 3, 1953

The retropinacolone rearrangement of several diarylalkylmethyl alkyl carbinols has been reported in the literature,[3] and in each case the symmetrical diaryldialkylethylene was obtained as the major product. By analogy to these compounds, the cyclic alcohols, 2,2-diphenylcycloheptanol (Ia) and 2,2-diphenylcyclohexanol (Ib), would be expected to produce the 1,2-diphenylcycloalkenes as the product of this type of reaction. On the other hand, Mueller and co-workers[4] have shown that 1,2-diphenylcyclohexene is unstable because of steric interference of the phenyl groups, and if 1,2-diphenylcyclohexene were formed, it could rearrange to the more stable 2,3-diphenylcyclohexene. Phenyl migration, however, might be retarded altogether in the retropinacolone rearrangement and the product of alkyl migration, cyclohexylidene diphenylmethane (IIa), would result. Thus a study of the retropinacolone rearrangement of two diphenyl cyclic alcohols was initiated in order to determine which of the groups migrated during the reaction and thus the influence of the cyclic system on the rearrangement.

The dehydration of 2,2-diphenylcycloheptanol (Ia) was effected by thermal dehydration on distillation at atmospheric pressure or by reagents such as phosphorus pentoxide, phosphorus tribromide or thionyl chloride. In each experiment the only product isolated, cyclohexylidene diphenylmethane (IIa), was that resulting from migration of the alkyl group. The identity of this material was confirmed by conversion to the epoxide.



Ia,b



IIa,b

a, $n = 5$
b, $n = 4$

2,2-Diphenylcyclohexanol (Ib) was dehydrated by treatment with phosphorus tribromide yielding cyclopentylidene diphenylmethane (IIb), identified by melting point and ultraviolet spectrum showing a maximum at 250 mμ with a molar extinction coefficient of 2.10×10^4. These values are quite similar to those obtained for cyclohexylidene diphenylmethane, maximum at 246 mμ with a molar extinction coefficient of 1.49×10^4. Thus the retropinacolone rearrangement proceeded with alkyl migrations in both cases. Unlike 2,2-diphenylcycloheptanol (Ia), the six-membered ring alcohol (Ib) was stable to atmospheric pressure distillation.

It is evident from these results that in the six- and seven-membered ring compounds studied ring contraction occurs in preference to migration of an aryl group. This preferential alkyl migration may well be related to the similar reaction noted in the pinacol rearrangement of unsymmetrical cyclic diaryl glycols.[5,6]

Experimental

Dehydration of 2,2-Diphenylcycloheptanol (Ia). a. With Phosphorus Pentoxide.—To 5.3 g. (0.02 mole) of 2,2-diphenylcycloheptanol[5] (Ia) in a 50-ml. round-bottom flask was added 3.0 g. (0.021 mole) of phosphorus pentoxide. The mixture was heated on a steam-bath for one hour and then treated with 100 ml. of cold water. The resulting white solid was removed by filtration yielding 3.7 g. (75%) of crude cyclohexylidene diphenylmethane (IIa) which, on recrystallization from low-boiling petroleum ether, melted at 82–83.5° and showed no depression of melting point on mixing with an authentic sample.

b. With Phosphorus Tribromide.—To 5.3 g. (0.02 mole) of molten 2,2-diphenylcycloheptanol (Ia) in a 50-ml. round-bottom flask was added dropwise 3.6 g. (0.014 mole) of phosphorus tribromide. After the vigorous reaction had subsided, the mixture was heated for an additional six hours on a steam-bath, poured into 200 ml. of water and the resulting solid removed by suction filtration. After two recrystallizations from ethanol, 2.3 g. (46%) of cyclohexylidene diphenylmethane (IIa), m.p. 81–83°, was obtained. This material showed no depression of melting point on mixing with an authentic sample.

c. With Thionyl Chloride.—Following the above procedure, 2.7 g. (0.01 mole) of Ia was treated with 1.2 g. (0.01 mole) of thionyl chloride. This reaction yielded 1.4 g. (56%) of product shown to be cyclohexylidene diphenylmethane (IIa) by mixture melting point.

d. By Distillation at Atmospheric Pressure.—After three consecutive distillations, b.p. 368–372°, 10.8 g. (0.04 mole) of Ia gave 8.8 g. of distillate. From a methanol solution this distillate deposited 3.6 g. (36%) of cyclohexylidene diphenylmethane (IIa), m.p. 82.8–83.6° after recrystallization from methanol. The oil remaining after removal of the methanol was oxidized with peracetic acid yielding 1.2 g. of crystalline cyclohexylidene diphenylmethane oxide. The total yield of IIa was 4.8 g. (48%). The remainder of the

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(2) These results were abstracted from the M.S. theses of N. B. Martin, Jr., and H. L. Fielding submitted to the faculty of the University of New Hampshire.

(3) J. Levy, *Bull. soc. chim.*, **29**, 878 (1921); R. Lucas and S. Legagneur, *ibid.*, **45**, 718 (1929); K. Sisido and H. Nozaki, THIS JOURNAL, **70**, 776 (1948).

(4) G. Mueller, J. Fleckenstein and W. Tallenn, *ibid.*, **73**, 2653 (1951).

(5) R. Lyle and G. Lyle, *ibid.*, **74**, 4059 (1952).

(6) A. Burger and W. Bennet, *ibid.*, **72**, 5414 (1950).

material could not be crystallized and was probably a mixture of Ia and IIa.

The Reaction of Cyclohexylidene Diphenylmethane (IIa) with Peracetic Acid.—To 2.5 g. (0.01 mole) of cyclohexylidene diphenylmethane (IIa) in 20 ml. of glacial acetic acid was added 0.3 g. of anhydrous sodium acetate in 2.5 g. of 45% peracetic acid. The mixture was stirred for two hours at which time all of the solid starting material was in solution. The reaction mixture was poured into 10 ml. of a saturated salt solution in water and the solid which precipitated was filtered by suction. The yield of cyclohexylidene diphenylmethane oxide was 2.5 g. (95%) and, on recrystallization from ethanol, melted 120.5–121°.[5] This material was identical with that obtained from the peracid oxidation of the retropinacolone rearrangement product.

2,2-Diphenylcyclohexanol (Ib).—A suspension of 0.8 g. (0.021 mole) of lithium aluminum hydride in 40 ml. of dry ether was prepared in a 200-ml. three-necked flask equipped for anhydrous conditions. To this mixture was added a solution of 5 g. (0.02 mole) of 2,2-diphenylcyclohexanone[6] in 15 ml. of ether. Very little heat was generated by the reaction. The mixture was stirred for one hour and water was added dropwise until no further reaction occurred. The mixture was then acidified with dilute sulfuric acid and the ether layer removed. The aqueous layer was extracted with an additional 25 ml. of ether and the organic layers combined and dried over sodium sulfate. On evaporation of the ether 4.6 g. (92%) of solid remained which, after recrystallization from ethanol, melted 82.5–83°. Because of the similarity in melting point with that of the starting material a mixture melting point was determined giving a value of 60–67°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.15; H, 7.91.

Dehydration of 2,2-Diphenylcyclohexanol (Ib). a. With Phosphorus Tribromide.—On treatment of 5.3 g. (0.021 mole) of molten 2,2-diphenylcyclohexanol (Ib) with 4.1 g. (0.015 mole) of phosphorus tribromide as described in (b) above, 3.8 g. (75%) of oil, b.p. 175–180° at 8 mm., was obtained. A portion of this oil was crystallized from petroleum ether using a Dry Ice-acetone bath. Recrystallization produced a white solid, m.p. 60.8–61.2°. These physical constants agree with those reported[7] for cyclopentylidene diphenylmethane (IIb), lit. b.p. 180–181° at 6–7 mm., m.p. 62–62.5°.

b. Attempted Dehydration on Distillation at Atmospheric Pressure.—After three consecutive distillations at atmospheric pressure 5 g. of Ib gave 4.68 g. of oil from which 3.71 g. (74%) of 2,2-diphenylcyclohexanol (Ib) was recovered.

The ultraviolet spectra of IIa and IIb were determined using a Beckmann Model DU quartz spectrophotometer. The concentrations of the solutions of IIa and IIb were 1.73 × 10^{-5} and 2.22 × 10^{-5} M, respectively, in 95% ethanol.

Acknowledgment.—The authors wish to express appreciation to Buffalo Electro-chemical Company, Inc., for generous supplies of peracetic acid used in this research.

[7] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946, p. 456.

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The Reaction of Sodium with Ethyl Trifluoroacetate

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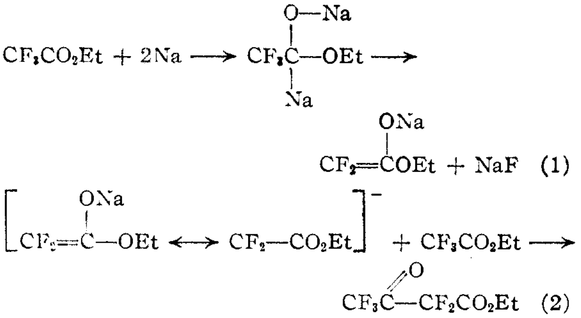
In an attempt to prepare a fluorine-containing acyloin, it was found that sodium reacted with ethyl trifluoroacetate in anhydrous ether yielding, on hydrolysis of the reaction mixture, ethyl γ,γ,γ-trifluoroacetoacetate in yields of 25–30%. A similar observation was made by Haszeldine[2] but no experimental details of explanations were offered. None of the expected acyloin was obtained and the only other products observed were unidentifiable high boiling materials, thought to be polymeric forms of 1,1,1,4,4,4-hexafluoroacetoin.

In an effort to delineate the reaction mechanism, ethyl pentafluoroacetoacetate[3] was treated with sodium under similar conditions and found to yield ethyl γ,γ,γ-trifluoroacetoacetate. This would indicate a possible reaction sequence which involves the formation of an intermediate acetoacetic ester. The latter compound could be obtained in the following manner



$$CF_3CO_2Et + 2Na \longrightarrow CF_3\overset{\overset{O-Na}{|}}{\underset{\underset{Na}{|}}{C}}-OEt \longrightarrow CF_2{=}\overset{\overset{ONa}{|}}{C}OEt + NaF \quad (1)$$

$$\left[CF_2{=}\overset{\overset{ONa}{|}}{C}-OEt \longleftrightarrow CF_2-CO_2Et\right]^- + CF_3CO_2Et \longrightarrow CF_3\overset{O}{\overset{\|}{C}}-CF_2CO_2Et \quad (2)$$

Corroborating evidence may be found in the fact that sodium fluoride was isolated from the reaction mixture in appreciable quantities and that only two moles of sodium per mole of ester was readily consumed.

Experimental

Ethyl Trifluoroacetate and Sodium in Anhydrous Ether.—A 500-ml., 3 necked flask was equipped with a sealed stirrer, a reflux condenser and an addition funnel with a side-arm pressure equalizer tube. The apparatus was flame-dried in a stream of dry nitrogen and one mole of sodium sand and 200 ml. of anhydrous ether were placed in the flask. One-half mole of ethyl trifluoroacetate (b.p. 60.5°, $n^{20}D$ 1.3073) was added dropwise to the stirred mixture of ether and sodium sand. After the first few ml. of ester had been added, the ether solution became dark red and the ether began to reflux vigorously. The remaining portion of the ester was added at such a rate that a steady reflux was maintained. After all the ester had been added, the mixture was stirred for an additional 2 hours. The ether solution was then poured over a mixture of 200 g. of crushed ice and 60 g. of concd. sulfuric acid. The ether layer was separated and the aqueous solution was extracted with ether. The ether solution was dried with anhydrous sodium sulfate and Drierite. After distillation of the ether, 20 g. of ethyl trifluoroacetate was recovered and 14 g. of ethyl γ,γ,γ-trifluoroacetoacetate was obtained boiling at 131–132°. A copper chelate was prepared, m.p. 188–189°.[4] The γ,γ,γ-trifluoroacetoacetic ester yielded 1,1,1-trifluoroacetone (b.p. 22°) upon hydrolysis with 30% sulfuric acid. A 2,4-dinitrophenylhydrazone was prepared, m.p. 139°.[4]

Anal. Calcd. for $C_9H_7F_3N_4O_4$: C, 37.0; H, 2.39. Found: C, 37.09; H, 2.52.

Sodium and Ethyl Pentafluoroacetoacetate in Anhydrous Ether.—A mixture of 70 ml. of anhydrous ether and 4.6 g. of sodium sand was placed in a 200-ml., 3-necked flask. A solution of 23 g. of ethyl pentafluoroacetoacetate and 50 ml. of anhydrous ether was added dropwise to the ether–sodium mixture. The ether solution was stirred for 6 hours and then poured over a mixture of 100 g. of crushed ice and 20 g. of concd. sulfuric acid. The ether layer was separated and the aqueous solution was extracted with ether.

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[1] Abstracted, in part, from the doctoral theses of H. W. Kilbourne and J. A. Barone, Purdue University.

[2] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

[3] E. T. McBee, O. R. Pierce, H. W. Kilbourne and E. R. Wilson, THIS JOURNAL, **75**, 3152 (1953).

[4] A. L. Henne, L. L. Quill, M. S. Newman and R. A. Staniforth, *ibid.*, **69**, 1819 (1947).