β,β-Dimethyl-δ,δ-diphenyl-δ-valerolactone[1]

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Stetter and Krause[2] described the preparation of a compound, m.p. 93°, believed to be 1,3-dibenzoyl-2,2-dimethylpropane, by a Friedel–Crafts condensation of 3,3-dimethylglutaryl chloride with benzene as well as by the action of phenylmagnesium bromide on diethyl 3,3-dimethylglutarate. The ketone formulation was supported by the reported formation of a bisdinitrophenylhydrazone of m.p. 196°.

Our inability to effect bromination of a material, prepared in accordance with their procedures and having the properties they describe, prompted a re-examintion of the structural assignment with an unequivocal outcome in favor of a lactone structure. The specimens prepared by the two different synthetic procedures were identical, by infrared and mixed melting point, and there is little likelihood therefore that the material is anything other than that described by Stetter and Krause despite a very minor discrepancy in melting point. The lactone function is clearly implicated by a carbonyl absorption at 1745 cm.$^{-1}$ and an n.m.r. spectrum showing two non-equivalent methylene groups. It was confirmed chemically by a positive hydroxamic test after reaction with hydroxylamine.[3] The formation of a bisdinitrophenylhydrazone could not be confirmed; the red solid produced in accordance with the published procedure was unchanged dinitrophenylhydrazine, not inconsistent with the reported melting point but in disagreement with the reported nitrogen analysis. It would have been surprising to encounter such easy formation of a bisdinitrohydrazone in a situation where a high degree of steric hindrance had to be invoked to explain the inertness of the compound to excess phenylmagnesium bromide. Accordingly, the evidence cited for a ketone function is discounted and it is proposed that the substance hitherto described as 1,3-dibenzoyl-2,2-dimethylpropane is in fact β,β-dimethyl-δ,δ-diphenyl-δ-valerolactone.

The formation of diketone in the analogous Friedel–Crafts condensation of glutaryl chloride with benzene, first established by Auger,[4] cannot be doubted. Although glutaryl chloride has the normal (acyclic) structure, according to Cason and Reist,[5] the intermediate δ-keto acid dichloride might be expected, if observations by the same authors[6] on δ-ketoenanthyl chloride are applicable, to cyclize readily. Evidently, under the reaction conditions, the δ-keto acid chloride is trapped by further conversion to diketone faster than it cyclizes. The chloride of 3,3-dimethylgluratic acid also has the normal structure, as shown by its n.m.r. spectrum. The appearance of lactone as the product of the Friedel–Crafts reaction, performed under comparable conditions, implies that the intermediate undergoes further condensation less readily as a consequence of the beta-substitution, or is more prone to cyclize. There is ample precedent for the operation of both effects.

Experimental

β,β-Dimethyl-δ,δ-diphenyl-δ-valerolactone.—The reaction of 3,3-dimethylglutaryl chloride (b.p. 95–96°/8 mm., $n^{25}\text{D}$ 1.4673) with benzene was performed by adding a solution of the chloride (20.8 g.) in benzene to a mixture of aluminum chloride (29.0 g.) and benzene (150 ml.) with stirring, at 0° during the addition, and thereafter at room temperature for 2 hr. Crushed ice and hydrochloric acid were added, and the combined benzene extracts were washed with dilute sodium carbonate solution and with water. Evaporation of the dried benzene solution produced a residual oil (20 g.) that partly crystallized. Yield was intentionally sacrificed, in an effort to achieve maximum purity, in two recrystallizations from petroleum ether to furnish 5.8 g. of product, m.p. 88–91°. The best analytical sample melted 91.7–92.2°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.41; H, 7.19. Found: C, 81.40; H, 7.23.

The Grignard synthesis followed the procedure of Stetter and Krause[2] on a smaller scale but with no attempt made to duplicate the reported yield of product. From 0.95 g. of diethyl 3,3-dimethylglutarate there was obtained 1.02 g. of crude product from which an analytical sample, m.p. 90.0–91.0°, was produced by recrystallization from petroleum ether. The sample was identical, by infrared and mixed melting point, with the product from the Friedel–Crafts reaction.

The infrared spectrum, 10% solution in carbon tetrachloride, showed carbonyl absorption at 1745 cm.$^{-1}$. For comparison the carbonyl absorption of δ-valerolactone in carbon tetrachloride occurs[7] at 1748 cm.$^{-1}$; the carbonyl of 1,3-dibenzoylpropane, in chloroform, absorbs[8] at 1683 cm.$^{-1}$.

Successive treatment[3] of the compound with hydroxylamine, hydrochloric acid, and ferric chloride produced the wine color characteristic of esters and lactones. Prolonged refluxing with 2,4-dinitrophenylhydrazine reagent effected no reaction, unchanged hydrazine being recovered.

N.m.r. Spectra.—Confirmation of the lactone structure is provided by the n.m.r. spectrum, taken in carbon tetrachloride, which shows the aryl multiplet at 2.51 τ, and three peaks, in area ratio of 1:1:3, at 7.39, 7.91, and 8.99 τ corresponding to the α-methylene, γ-methylene, and *gem*-dimethyl hydrogens.

The n.m.r. spectrum of 3,3-dimethylglutaryl chloride, in carbon disulfide solution, exhibited peaks at 6.90 and 9.05 τ in an area ratio of 2:3. Upon addition of aluminum chloride two liquid phases appeared and the n.m.r. peaks, including that of the tetramethylsilane standard, exhibited doubling but were otherwise unchanged. Diethyl 3,3-dimethylglutarate showed a quartet (J = 6.8 c.p.s.) centered at 4.97 τ (O-methylene), peaks at 7.66 τ (α-methylene) and 8.92 τ (*gem*-dimethyl) in an area ratio of 2:3, and a triplet centered at 8.76 τ, (methyl hydrogens in ethyl groups) partially masked by the 8.92 peak.

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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Pinacol Reduction of 1,2-Dibenzoylethane. Formation of a Strained Cyclic Pinacol

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In connection with recent studies on the cleavage of 1,4-diketones under pinacol conditions,[1] we have observed that 1,2-dibenzoylethane (I) is converted to

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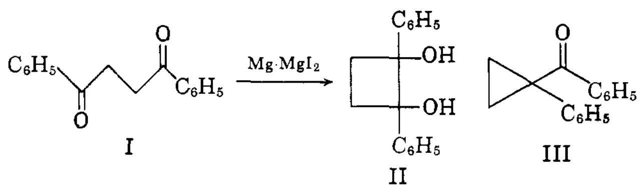
[1] G. W. Griffin and R. B. Hager, in press.

trans-1,2-diphenylcyclobutane-1,2-diol (II) by the action of magnesium–magnesium iodide couple.[2] It has been reported that this transformation may be achieved electrolytically although no attempt was made to isolate and characterize the presumed product.[3]



Treatment of I with the Gomberg couple in tetrahydrofuran at the reflux temperature provided II. Especial care was exercised in the preparation and utilization of the magnesium–magnesium iodide couple. The reaction was conducted in freshly dried solvents under a blanket of prepurified nitrogen.

Acetophenone, a minor by-product in the reaction ($<5\%$), was detected by gas chromatography and presumably is formed by homolytic fragmentation of the intermediate 1,4-diketyl.[4]

The structure of II was established by elemental analysis, molecular weight determination, and infrared as well as n.m.r. analysis.

The infrared spectrum of II determined in carbon tetrachloride exhibits the characteristic bonded and nonbonded O—H stretch bands at 3520 and 3596 cm.$^{-1}$ respectively.[5] The assignment of *trans* stereochemistry to the glycol II is based upon infrared dilution studies which demonstrate that intermolecular hydrogen bonding is responsible for the absorption at 3520 cm.$^{-1}$.

The n.m.r. spectrum of II (deuterioacetone) is entirely consistent with the assigned structure and shows a peak at $\tau = 5.97$ (OH) as well as an A_2B_2 multiplet centered at $\tau = 7.52$ (CH_2). In addition there is a complex array of peaks centered at $\tau = 2.93$ in the spectrum of II arising from the aromatic protons. The relative peak areas are in agreement with the proposed structure.

Conclusive evidence for the structure of the 1,2-diol was obtained from oxidative cleavage with lead tetraacetate which gave I.[6]

The rearrangement of II in 20% sulfuric acid appears to occur exclusively with ring contraction to 1-phenyl-1-benzoylcyclopropane (III). The infrared spectrum of III exhibits a strong band at 1675 cm.$^{-1}$ and this compares favorably with the value of 1673 cm.$^{-1}$ (CCl_4) reported for cyclopropyl phenyl ketone.[7] The n.m.r. spectrum of III determined in carbon tetrachloride shows an A_2B_2 multiplet centered at $\tau = 8.6$ (CH_2) which is near the value of 8.7 observed for the methylene hydrogens of 1,1-dicarbethoxycyclopropane. In addition there is a complex series of peaks due to aromatic hydrogens centered at $\tau = 2.6$. The ratio of peak areas is 1.0:2.4 compared with a theoretical value of 1.0:2.5. Close scrutiny of the infrared spectrum of the *crude* rearrangement product did not reveal any absorption in the 1700–2000-cm.$^{-1}$ region which would be expected if phenyl migration to give 2,2-diphenylcyclobutanone had occurred.[8] The rearrangement of the *trans*-pinacol II is in accord with the behavior of *trans*-1,2-dimethylcyclohexane-1,2-diol.[9] In both cases ring contraction is the preferred route. It is of interest that while *cis*-1,2-dimethylcyclopentane-1,2-diol is rearranged smoothly to the corresponding cyclopentanone the *trans* isomer suffers resinification under rearrangement conditions.[10]

Experimental

***trans*-1,2-Diphenylcyclobutane-1,2-diol (II).**—A suspension of 0.73 g. (0.03 g.-atom) of magnesium powder and 3.84 g. (0.015 mole) of iodine in 125 ml. of dry tetrahydrofuran was stirred for 5 hr. at 80°. To the resulting maroon reaction mixture was added, by extraction from a thimble, 1.00 g. (4.3 mmoles) of dibenzoylethane.[11] During the course of the addition and subsequent reflux period (30 hr.) the reaction mixture was protected by an atmosphere of nitrogen prepurified by treatment in turn with Fieser's solution[12] and concentrated sulfuric acid. The mixture was finally hydrolyzed with 15 ml. of water and the volatile solvents removed under reduced pressure. The residue was then extracted repeatedly with benzene and the combined extracts were treated with Norit and dried over calcium sulfate. Concentration of the benzene solution provided 0.3 g. (30%) of II which was recrystallized from methylcyclohexane (m.p. 148–150°). The yield of II was extremely variable. When the reaction was scaled up tenfold the yield of II dropped to 1%.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; mol. wt., 240. Found: C, 80.05; H, 6.89; mol. wt., 259 (Rast).

The infrared spectrum of II (KBr) exhibits significant absorption bands at 3470 (m), 3380 (s), 3096 (w), 3072 (w), 3032 (w), 3000 (w), 2960 (w), 1496 (m), 1450 (s), 1380 (m), 1365 (m), 1132 (s), 1070 (s), 972 (m), 933 (s), 910 (s), 775 (s), and 700 (s) cm.$^{-1}$.

Lead Tetraacetate Oxidation of 1,2-Diphenylcyclobutane-1,2-diol (II).—To 0.1 g. (0.42 mmole) of the diol and 0.125 g. (0.95 mmole) of anhydrous potassium carbonate suspended in 10 ml. of benzene was added 0.18 g. (0.42 mmole) of lead tetraacetate which had been washed with ethanol followed by hexane to remove acetic acid. The resulting mixture was heated at the reflux temperature for 2 hr. and subsequently filtered. When the filtrate was concentrated under reduced pressure colorless crystals were deposited (m.p. 147–148°, lit.,[11] m.p. 144–145°). The infrared spectrum of this oxidation product was identical with that of an authentic sample of 1,2-dibenzoylethane.

***Pinacol Rearrangement of* 1,2-Diphenylcyclobutane-1,2,-diol (II).**—A mixture of 0.20 g. (0.84 mmole) of II and 5 ml. of 20% sulfuric acid was heated under reflux for 3 hr. During this period the suspended solid was transformed into a yellow oil. The reaction mixture was cooled and then extracted repeatedly with benzene. The combined benzene extracts were washed with saturated sodium bicarbonate and then dried over Drierite. Evaporation of the solution under reduced pressure afforded 0.19 g. of crystalline product. Recrystallization of this product from methanol at −50° yielded colorless crystals, m.p. 71–72°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.42; H, 6.26.

Absorption bands in the infrared spectrum of the rearrangement product were observed at 3085 (w), 3065 (w), 3030 (w), 1660 (s), 1500 (m), 1300 (m), 1275 (m), 1200 (m), 1180 (m), 990 (m), 760 (m), and 700 (s) cm.$^{-1}$.

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