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.