157. *Benzoylphenacylcarbinol.*

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REQUIRING recently some phenylglyoxal for enzyme experiments, we prepared the compound by the excellent method of Riley *et al.* (J., 1932, 1875). After removal of the glyoxal from the reaction mixture by thorough extraction with hot water, the residual acetophenone, on keeping, deposited a substantial amount of crystalline material. This proved to be a hitherto undescribed 1 : 4-diketone, *benzoylphenacylcarbinol,* $C_6H_5{\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$, which, as we showed by synthesis, is formed by the combination of 1 mol. of phenylglyoxal with 1 mol. of acetophenone.

We established the presence of the hydroxyl group by preparing the *acetate,* and of the two carbonyl groups by the action of hydroxylamine on the carbinol. To our surprise, however, the dioxime which we isolated was not that of the original substance but of diphenacyl, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$; and we obtained confirmatory evidence of this somewhat remarkable reduction of the secondary alcoholic group to the methylene group by means of hydroxylamine when in another experiment with hydroxylamine we obtained a small amount of diphenacyl itself.

Numerous attempts to oxidise benzoylphenacylcarbinol to the corresponding known tetraketone were unsuccessful. Nitric acid converted it into benzoic acid ; chromic acid or permanganate under various conditions produced amorphous coloured products. Benzoylphenacylcarbinol reacts with ammonia in acetic acid solution, yielding at least two crystalline substances.

It gives a characteristic colour reaction when dissolved in concentrated sulphuric acid. An intense emerald-green solution is first produced, which eventually changes to a deep red. Diphenacyl gives with concentrated sulphuric acid a much fainter apple-green colour, passing through a fluorescent olive-green stage to a final red (cf. Kapf and Paal, *Ber.*, 1888, **21**, 3056).

EXPERIMENTAL.

Isolation of Benzoylphenacylcarbinol from the Reaction Mixture of Riley et al. (loc. cit.).—220 G. of acetophenone were boiled under reflux with 100 g. of SeO_2 for 2¼ hr. Phenylglyoxal was removed by shaking the reaction mixture (decanted from the Se formed) repeatedly with hot H_2O; 130 g. of phenylglyoxal hydrate were obtained. The residual acetophenone was reduced to small bulk by distillation in a vac. and kept at 4°. The crude crystals obtained from this liquid were recrystallised from EtOH, separating in colourless platelets (27·8 g.), m. p. 98° [Found : C, 75·7; H, 5·5; *M* (Rast), 250. $C_{16}H_{14}O_3$ requires C, 75·6, H, 5·5% ; *M*, 254]. The compound crystallises from AcOEt and from H_2O, in which it is slightly sol., as platelets, and from C_6H_6 and ligroin as prismatic needles.

Preparation of Benzoylphenacylcarbinol from Phenylglyoxal and Acetophenone.—2 G. of phenylglyoxal hydrate in 30 g. of acetophenone were boiled under reflux for 15 min. The excess of acetophenone was then removed in a vac. and the residual oil was kept at 4°. The crude benzoylphenacylcarbinol which crystallised, after draining on porous pot, weighed 3·2 g. and was recrystallised first from EtOH and then from ligroin. It was identical with the compound described above.

Benzoylphenacylcarbinyl Acetate.—1 G. of the carbinol was heated on the boiling water-bath with 20 c.c. of Ac_2O for 2 hr. Excess of Ac_2O having been removed in a vac., the oily residue was dissolved in EtOH and warmed at 65° for 10 min. The EtOH was then removed in a vac., and the process repeated. The final oily residue was washed twice with H_2O and then dissolved in hot 96% EtOH, from which crystals separated. After recrystallising thrice from 96% EtOH, the *acetate* was obtained pure as prisms, m. p. 120° (Found : C, 72·9 ; H, 5·35. $C_{18}H_{16}O_4$ requires C, 72·9 ; H, 5·4%).

Action of Hydroxylamine on Benzoylphenacylcarbinol.—This reaction is complex, and the products obtained vary with the conditions of expt.

When 1 mol. of the carbinol was heated with 2 mols. of NH_2OH,HCl in alc. solution the liquid immediately developed a deep red colour which rapidly changed to dark green. On repeating the expt. in the presence of NaOAc no coloration appeared, but only uncrystallisable resinous products resulted. On repeating it in the presence of $BaCO_3$ colourless resinous products were still obtained, but a small amount of the dioxime of diphenacyl was isolated (a), while the action of free NH_2OH produced a small quantity of diphenacyl itself (b).

(a) 1·1 G. of NH_2OH,HCl were boiled under reflux on the water-bath in 40 c.c. of EtOH in the presence of 3 g. of $BaCO_3$ for 15 min. 2 G. of benzoylphenacylcarbinol in 20 c.c. of EtOH were then added and the mixture was boiled for 45 min. After filtration and evaporation in a vac. to half its vol. the solution was heated and H_2O was added until a persistent turbidity resulted. On keeping, the liquid deposited 0·4 g. of cryst. material. This was purified by four crystns. from EtOH and gave stout prisms, m. p. 206—208° (cf. Kapf and Paal, *Ber.*, 1888, **21**, 3057) [Found: C, 71·7; H, 6·0; N, 10·7; *M* (Rast), 263. Calc. for $C_{16}H_{16}O_2N_2$: C, 71·7; H, 6·0; N, 10·4%; *M*, 268].

(b) 1 G. of benzoylphenacylcarbinol was boiled in 45 c.c. of EtOH containing 0·26 g. of NH_2OH in the presence of a small amount of K_2CO_3 under reflux for 1 hr. H_2O was added to the red reaction mixture, and then dil. HCl until the reaction was just acid to litmus. A cryst. substance contaminated with oily material separated (0·25 g.). After recrystn. once from EtOH and twice from 96% EtOH, long slender needles were obtained, m. p. 148° (Found: C, 80·6; H, 6·0. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%). The substance was N-free and gave the characteristic colour reaction of diphenacyl with conc. H_2SO_4. The unexpected nature of the compound made it desirable to compare it directly with authentic diphenacyl. This compound was therefore synthesised from ω-bromoacetophenone (Fritz, *Ber.*, 1895, **28**, 3032) and the identity of the substance was completely confirmed by mixed m. p., cryst. form, solubility, and colour reaction.

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