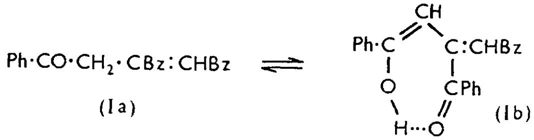
89. *Structure and Synthesis of Kostanecki's Compound, m. p.* 120°.

By P. F. DEVITT, (MRS.) E. M. PHILBIN, and T. S. WHEELER.

The substance $(C_8H_6O)_x$ obtained by the base-catalysed self-condensation of ω-phenoxyacetophenone is 1 : 2 : 3-tribenzoylpropene. An unambiguous synthesis of this olefin is provided by the action of bromine on 1 : 2 : 3-tribenzoylpropane.

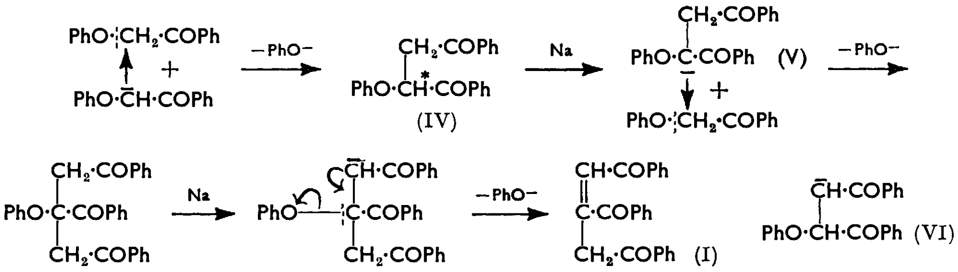
KOSTANECKI and TAMBOR[1] were unable to assign a structure to an orange compound $(C_8H_6O)_x$ (I), m. p. 120°, which they obtained by the sodium-catalysed condensation of ω-phenoxyacetophenone. It has now been found that this substance is also obtained by base-condensation of ω-*p*-chlorophenoxyacetophenone, so that the aryloxy-group is eliminated in the reaction. Further, as Kostanecki and Tambor[1] showed, the orange compound (I) can be reduced to a colourless product which has now been identified as 1 : 2 : 3-tribenzoylpropane, $CHBz(CH_2Bz)_2$, previously obtained by Lutz and Palmer[2] from acetophenone and dibenzoylethylene. Treatment of the triketone with bromine yielded an unstable bromo-compound which lost hydrogen bromide with production of the orange compound (I). This reaction constitutes an unambiguous synthesis of Kostanecki's compound.



Compound (I) is, accordingly, 1 : 2 : 3-tribenzoylpropene. As the enol form (Ib), it formed monomethyl and monoacyl derivatives, Ph·C(OR):CH·CBz:CHBz (III; R = Me or acyl). Infrared spectra confirmed the structure (I) (cf. Table). The ultraviolet absorption maximum in ethanol for compound (I) (257 mμ) showed a bathochromic shift as compared with the maxima for acetophenone (240 mμ) and ω-phenoxyacetophenone (243 mμ).

A possible alternative to the condensation mechanism suggested by Yates and his colleagues[3] is:

$$2Ph{\cdot}CO{\cdot}CH_2{\cdot}OPh + 2Na \longrightarrow 2[(Ph{\cdot}CO{\cdot}\bar{C}H{\cdot}OPh)Na^+] + H_2$$



It is assumed that the compound (IV) reacts with sodium to give the ion (V) rather than (VI). The phenoxyl group is electrophilic so that the hydrogen atom (H*) in (IV) is the more likely to be replaced.

The reaction is not general since no useful result was obtained in attempts to condense

---

[1] Kostanecki and Tambor, *Ber.*, 1902, **35**, 1679.

[2] Lutz and Palmer, *J. Amer. Chem. Soc.*, 1935, **57**, 1952.

[3] Yates, Farnum, and Stout, *Chem. and Ind.*, 1956, 821.

ω-hydroxyacetophenone, ω-phenoxy-*p*-phenylacetophenone, or *p*-bromo-ω-phenoxyacetophenone in the presence of sodamide. 1 : 2-Di-*p*-bromobenzoylethane[4] was an unexpected by-product in the preparation of the last compound from *p*ω-dibromoacetophenone and phenol.

Infrared bands (cm.$^{-1}$).

1 : 2 : 3-Tribenzoylpropene in KBr	
Conjug. C:O	1622
C:C·C:O or CO·C[CH:C(OH)]:C·C:O	1596, 1578(s), 1534—1528(s)
$CO·CH_2$	1416
Ph, probably monosubst.	1490, 1451, 1179(s), 1051(s), 962(s), 761(s), 680(s)

p-$NO_2·C_6H_4·CO·O·CPh:CH·CBz:CHBz$ in $CHCl_3$	
Conjug. C:O	1665, 1647
CO·O·C:C	1742(s)
NO_2 (probably incl. conjug. C:C)	1556(s), 1345(s)
p-$NO_2·C_6H_4·CO·O$	1276, 1230(s), 1072(s)
p-Disubstn.	780, 690(s)

1 : 2 : 3-Tribenzoylpropene in $CHCl_3$	
Conjug. C:O	1666(s) (sh 1682)
C:C·C:O	1597, 1578
Assoc. OH (probably H-bonded)	3556(w)
Ph	1485, 1450

EXPERIMENTAL

Crystallisation was from ethanol unless otherwise stated.

1 : 2 : 3-*Tribenzoylpropene*.—A stirred solution of ω-phenoxyacetophenone (10 g.) in xylene (70 ml.) was treated with granulated sodium (1 g.) and kept at 50° until dissolution of the metal was complete. The mixture was acidified with acetic acid and treated with ether. 1 : 2 : 3-*Tribenzoylpropene* was extracted from the non-aqueous layer by dilute aqueous sodium hydroxide from which it was precipitated by carbon dioxide. It crystallised in orange needles (1 g.), m. p. 121—123° (Found: C, 81·1; H, 5·3. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%). Kostanecki and Tambor[1] gave m. p. 120° for their " orange " compound.

A mixture of ω-*p*-chlorophenoxyacetophenone[5] (13 g.), ether (200 ml.), powdered sodamide[3] (4·3 g.), and methanol (2 drops) was refluxed for 2 hr. under nitrogen. 1 : 2 : 3-Tribenzoylpropene (mixed m. p. confirmation) was recovered from the acidified product as described above. The yield of crystallised material was 2·2 g.

Bromine (0·5 g.) in glacial acetic acid (5 ml.) was added dropwise with stirring to a cooled suspension of 1 : 2 : 3-tribenzoylpropane[2] (1 g.) in the same solvent (10 ml.). 1 : 2 : 3-Tribenzoylpropene (mixed m. p.; yield of crystallised product, 0·1 g.) was precipitated when the mixture was warmed and added to water.

Reduction of 1 : 2 : 3-*Tribenzoylpropene*.—A mixture of the tribenzoylpropene (1 g.), ethanol (10 ml.), and sodium dithionite (0·6 g.) was refluxed for 2 hr. and filtered. The filtrate was acidified with glacial acetic acid and diluted with water to turbidity. 1 : 2 : 3-Tribenzoylpropane, which separated on cooling, formed prisms (0·8 g.), m. p. and mixed m. p. with an authentic specimen[2] 124—125° (Found: C, 81·2; H, 5·7. Calc. for $C_{24}H_{20}O_3$: C, 80·9; H, 5·7%). The reduction was also effected by zinc and dilute ethanolic acetic acid.[6]

Tribenzoylpropene with dimethyl sulphate and aqueous sodium hydroxide furnished 3 : 4-*dibenzoyl*-1-*methoxy*-1-*phenylbutadiene* (III; R = Me), yellow needles, m. p. 166° (Found: C, 81·7; H, 5·6; OMe, 8·6. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·5; OMe, 8·4%). The propene derivatives with pyridine and benzoyl chloride gave 3 : 4-*dibenzoyl*-1-*benzoyloxy*-1-*phenylbutadiene* (III; R = Bz) which was insoluble in the usual solvents. It was purified by washing it with boiling ethanol and was obtained in grey crystals, m. p. 212° (Found: C, 81·4; H, 4·7. $C_{31}H_{22}O_4$ requires C, 81·2; H, 4·8%). 3 : 4-*Dibenzoyl*-1-p-*nitrobenzoyloxy*-1-*phenylbutadiene* (III; R = *p*-nitrobenzoyl), crystallised in needles, m. p. 207° (Found: C, 74·4; H, 4·1; N, 3·1. $C_{31}H_{21}O_6N$ requires C, 74·0; H, 4·2; N, 2·8%). 3 : 4-*Dibenzoyl*-1-*furoyloxy*-1-*phenylbutadiene* (III; R = furoyl) formed yellowish-brown crystals, m. p. 158—160° (Found: C, 78·1; H, 4·5. $C_{29}H_{20}O_5$ requires C, 77·7; H, 4·5%).

ω-*Phenoxy*-p-*phenylacetophenone*, which crystallised in plates, m. p. 91° (Found: C, 83·3;

---

[4] Conant and Lutz, *J. Amer. Chem. Soc.*, 1925, **47**, 891.

[5] Wright and Lincoln, *ibid.*, 1952, **74**, 6301.

[6] Cf. Iyer, Shah, and Venkataraman, *Proc. Indian Acad. Sci.*, 1951, **33**, *A*, 120.

H, 5·7. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·5%), was prepared from ω-bromo-*p*-phenylacetophenone[7] and phenol in aqueous sodium hydroxide.[8]

1 : 2-*Di*-p-*bromobenzoylethane and* p-*Bromo*-ω-*phenoxyacetophenone.*—A mixture of *p*ω-dibromoacetophenone[9] (75 g.), phenol (26 g.) and 10% aqueous sodium hydroxide (100 ml.) was refluxed for 3 hr. Fractional crystallisation of the solid product from glacial acetic acid gave a first crop of 1 : 2-di-*p*-bromobenzoylethane which separated in plates (3 g.), m. p. 182°, not depressed by the addition of an authentic sample[4] (Found: C, 48·4; H, 2·9. Calc. for $C_{16}H_{12}O_2Br_2$: C, 48·5; H, 3·0%). The *bis*-2 : 4-*dinitrophenylhydrazone* formed orange crystals, m. p. 248—250° (decomp.) (Found: C, 43·9; H, 2·9; H, 14·5; Br, 20·8. $C_{28}H_{20}O_8N_8Br_2$ requires C, 44·4; H, 2·6; N, 14·9; Br, 21·2%).

The second crop (p-*bromo*-ω-*phenoxyacetophenone*) separated in needles (48 g.), which on further crystallisation had m. p. 90—91° (Found: C, 57·7; H, 3·8; Br, 27·7. $C_{14}H_{11}O_2Br$ requires C, 57·7; H, 3·8; Br, 27·5%).

Professor Peter Yates and his colleagues[3] arrived independently at the structure of Kostanecki's compound. We acknowledge their priority in obtaining confirmatory evidence. We appreciate their agreement to simultaneous publication of preliminary notes.[3, 10]

One of us (P. F. D.) thanks Dr. Michael J. Walsh and University College, Dublin, for the award of a Michael J. Walsh Research Fellowship. Grateful acknowledgment is also made to Professor Hs. H. Günthard, Eidg. Technische Hochschule, Zürich, and Professor Wesley Cocker and Mr. E. R. Stuart, Trinity College, Dublin, for providing the infrared determinations and assisting in their interpretation. The authors also thank a Referee for valuable suggestions relative to the reaction mechanism discussed in this paper.

UNIVERSITY COLLEGE, DUBLIN.

[*Received, September* 18*th*, 1957.]

[7] Carpenter and Turner, *J. Chem. Soc.*, 1934, 869.

[8] Möhlau, *Ber.*, 1882, **15**, 2497.

[9] Langley, *Org. Synth.*, 1946, Coll. Vol. I, p. 127.

[10] Devitt, Philbin, and Wheeler, *Chem. and Ind.*, 1956, 822.