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CONDENSATION OF 2-BENZOYLBENZOIC WITH PHENYLACETIC ACID

A NEW SIMPLE ROUTE TO PENTAPHENE*

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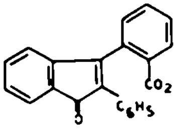
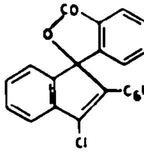
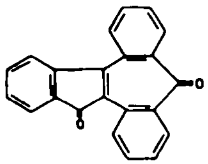
Abstract--The reaction of 2-benzoylbenzoic acid with phenylacetic acid in the presence of phosphorus pentachloride gives spiro[3-chloroindene-1,1'-phthalane-3'-one] (II) and 9H,14H-tribenz[*a.e.h*]azulene-9,14-dione (III). The latter compound can be easily converted into pentaphene.

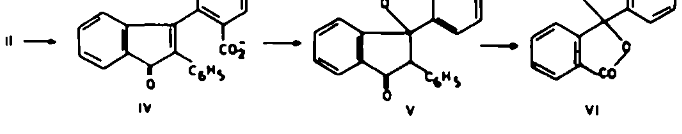
During the synthesis of 2-aryl-3-phenylindones,[2] the condensation between 2-benzoylbenzoic and phenylacetic acid in the presence of phosphorus pentachloride was tried as a possible route to the indone I. However, fractional crystallization of the reaction mixture gave, instead of the expected chloride of acid I, two products to which structures II and III were respectively assigned.


I


II


III

The IR spectrum of the spiro derivative II shows a carbonyl stretching absorption band at 5·73 μ typical of a five-membered lactone. Treatment of II with boiling ethanolic potassium hydroxide produced a red solution containing ion IV. Acidification of the solution gave a gummy red precipitate which solidified rapidly on treatment with acetic acid. The pure colorless product V was obtained on further crystallization of this material from benzene-hexane. Compound V is slowly dissolved by aqueous sodium hydroxide (rapidly by ethanolic potassium hydroxide) to give a red solution containing again IV, which shows an electronic spectrum quite similar to that of 2,3-diphenylindone. The IR spectrum of V shows two carbonyl stretching absorption bands at 5·63 (five-membered lactone) and 5·83 μ (ketone). Oxidation of V with potassium permanganate afforded the known[3] 1,1'-spirobiphthalane-3,3'-dione (VI).


IV V VI

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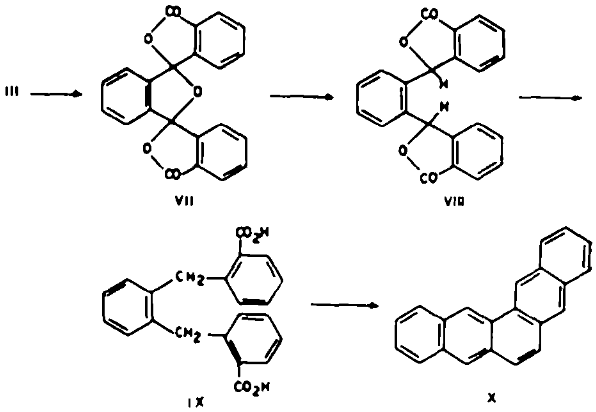
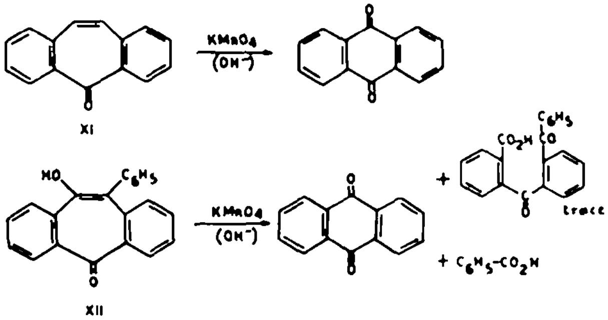
* Dedicated to Prof. Remo de Fazi on his 75th birthday. Preliminary note published in *Tetrahedron Letters* 3023 (1965).

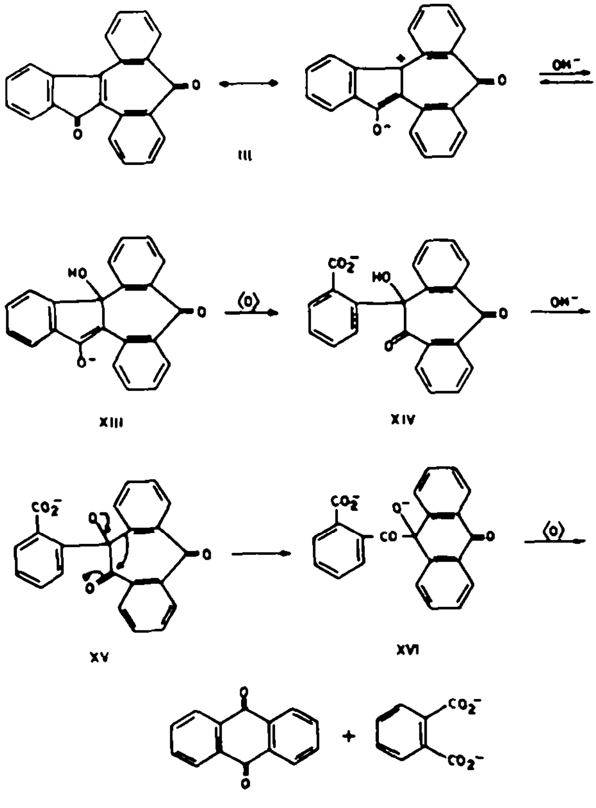
[1] Abstracted from the Doctoral Thesis of M. Isola.

[2] A. Marsili and M. Isola, *Ann. Chim. Rome* in press.

[3] C. Graebe and P. Juillard, *Liebigs Ann.* 242, 214 (1887).


III
VII
VIII
IX
X
CO
O
H
CH2
CO2H


XI
KMnO4
(OH⁻)
XII
HO
C6H5
CO2H
CO
trace
+ C6H5-CO2H


III
OH⁻
XIII
HO
O⁻
(O)
XIV
CO2⁻
XV
XVI
CO

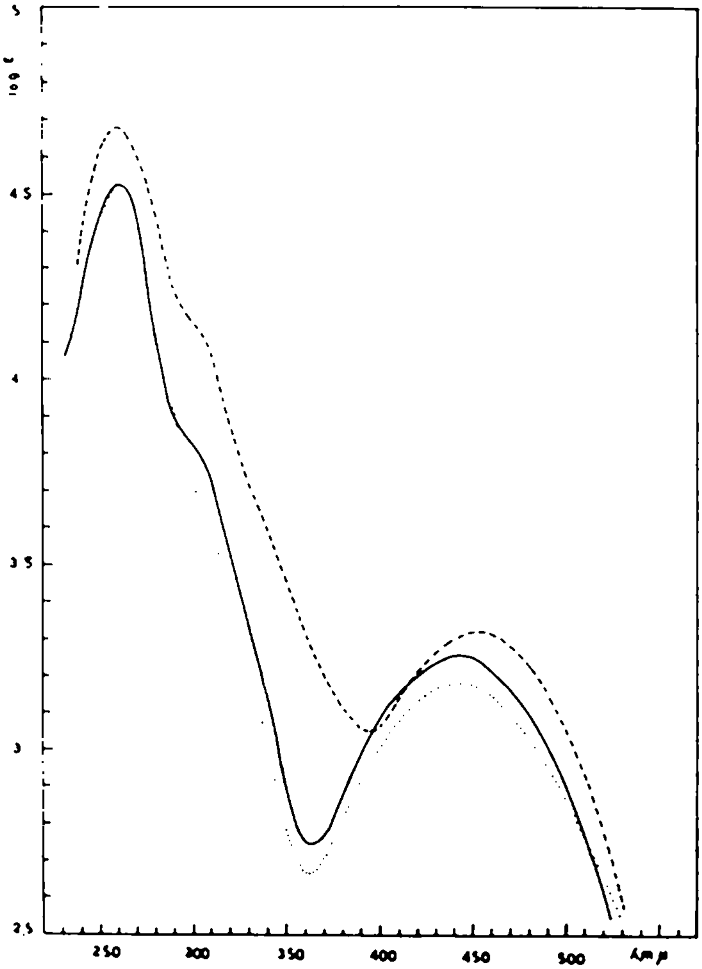


FIG. 1. Spectra of: 2,3-diphenylindone (——); III (——) and IV (. . . .).

The IR spectrum of III shows two carbonyl stretching absorption bands at 5·86 (indone carbonyl) and 6·04 μ (cross-conjugated ketone). The product has an electronic spectrum quite similar to that of 2,3-diphenylindone.

Oxidation of III with potassium permanganate in acetone solution gave the known dispiro derivative VII which was successively converted, by the method described by Clar,[4] into the diphthalidylbenzene VIII, the dicarboxylic acid IX and pentaphene (X).

The oxidation of III with potassium permanganate in aqueous basic suspension gave rather surprising results: anthraquinone and phthalic acid were obtained in almost quantitative yield.

Similar types of transformations are known in the field of tropolone derivatives.[5,6] We have also observed the formation of anthraquinone in the analogous oxidation of

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[4] E. Clar and D. G. Stewart, *J. Chem. Soc.* 3215 (1951); see also: R. Weiss and S. R. Kratz, *Monatsh.* **50**, 429 (1928).

[5] P. L. Pauson, *Chem. Rev* **55**, 9 (1955).

[6] J. Rigaudy and L. Nedelec, *Bull. Soc. Chim. Fr* 659 (1959).

dibenz[*a*,*e*]tropone (XI), whereas anthraquinone and benzoic acid have been obtained from 5-hydroxy-6-phenyldibenz[*a*,*e*]tropone (XII).

It appears likely that the contraction of the seven-membered ring in III involves an alkali-promoted rearrangement of an oxidation intermediate, as exemplified in XIII → XVI. The first step of this transformation might be the addition of base at the β-position of the indenone double bond, with formation of the intermediate XIII. Similar additions are indeed known to occur for 2-cyano-3-phenylindone[7] and ethyl 3-phenylindone-2-carboxylate.[8] Additional support for an analogous behaviour of III toward nucleophiles was provided by the separation of a labile adduct in the treatment of the compound with aqueous methylamine.

Oxidation of XIII and subsequent rearrangement may lead to the final products.

EXPERIMENTAL

All m.p. (Kofler hot stage, and not corrected). IR (on nujol mulls on a Perkin-Elmer "Infracord" model 137 spectrophotometer). UV (in 95% EtOH using a Beckman model DU apparatus). Identity of compds was verified, when possible, by mixed m.ps. and IR spectra.

Condensation between 2-benzoylbenzoic and phenylacetic acid. A mixture of 2-benzoylbenzoic acid (22·6 g; 0·1 mole), phenylacetic acid (13·6 g; 0·1 mole) and PCl_5 (20·8 g; 0·1 mole) was heated for 50 min in an oil bath at 140–150°. After cooling to room temp the mixture was extracted successively with 100 ml and 200 ml boiling AcOH. The first extract was discarded. From the second, 8·4 g brown soild separated on cooling. The residue of the extraction, on crystallization from AcOH, afforded 7·6 g III as orange-red needles. The mother liquor of this recrystallization was used to crystallize the 8·4 g of brown solid, thus obtaining, after a further crystallization from AcOH, 4 g III. All the mother liquors were combined and allowed to stand; after 2 days 1·6 g II separated out as light yellow plates. The fractions, obtained by successive concentrations, were combined and crystallized fractionally from benzene to give 2·2 g II, 1·2 g III and 2·6 g mixture. An analytical sample of II (spiro[3-chloroindene-1,1′-phthalane-3′-one]) had m.p. 282–285°, λ_{CO} 5·73 μ, after crystallization from AcOH. (Found: C, 76·26; H, 3·96. $C_{22}H_{13}ClO_2$ requires: C, 76·63; H, 3·80%.) Compd III (9H, 14H-tribenz[*a.e.h*]azulene-9,14-dione), after successive crystallizations from AcOH and benzene, had m.p. 239–240°, λ_{CO} 5·86, 6·04 μ, λ_{max} 258, 298 (shoulder), 450 mμ, log ϵ 4·68, *ca.* 4·15, 3·32. (Found: C, 85·72; H, 4·05. $C_{22}H_{12}O_2$ requires: C, 85·70; H, 3·92%.) By stirring the product with 40% aq methylamine, a white solid was obtained, which on washing with water, transformed slowly to III. The dioxime, prepared according to Shriner *et al.*,[9] melted at 234–235° after crystallization from MeOH. (Found: N, 8·00. $C_{22}H_{14}N_2O_2$ requires: N, 8·28%.)

Treatment of II *with alkali.* A soln of II (0·3 g) in 10% ethanolic KOH (10 ml) was refluxed for 15 min. On dilution with water and acidification of the red soln with dil. HCl, a gummy red ppt formed. The supernatant liquid was discarded and the residue was successively crystallized from AcOH and benzene–hexane to afford V as plates (0·15 g), m.p. 188–190°, λ_{CO} 5·63, 5·83 μ. (Found: C, 80·85; H, 4·44. $C_{22}H_{14}O_3$ requires: C, 80·97; H, 4·32%.) The product is insoluble in Na_2CO_3 aq but dissolves in ethanolic KOH or in hot NaOH aq giving a red soln. UV of V (0·1N ethanolic KOH): λ_{max} 265, *ca.* 300 (inflection), 444 mμ, logϵ 4·57, *ca.* 3·70, 3·18.

Oxidation of V *with* $KMnO_4$. A mixture of V (0·1 g), $KMnO_4$ (0·1 g) and 0·2N Na_2CO_3 (10 ml) was refluxed for 30 min. A little MeOH was added to eliminate the excess $KMnO_4$, the soln was filtered, acidified, heated to boiling for 30 min, then extracted with ethyl ether. The residue obtained on evaporation of the extract was heated 5 min on a steam bath with 0·1N $NaHCO_3$. The undissolved material (30 mg) was identified as 1,1′-spirobiphthalane-3,3′-dione (VI).[8]

Oxidation of III *with* $KMnO_4$ *in acetone.* A soln of III (3 g) and $KMnO_4$ (5 g) in acetone (200 ml) was refluxed for 1·5 hr. The excess $KMnO_4$ was destroyed with MeOH, the acetone was evaporated off, and the residue was extracted with boiling 1N NaOH (60 ml). The filtered soln was acidified

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[7] A. Marsili, *Ann. Chim. Rome* **51**, 237 (1961).

[8] C. F. Koelsch, *J. Org. Chem.* **25**, 2088 (1960).

[9] R. L. Shriner, R. C. Fuson and D. Y. Curtin, *The Systematic Identification of Organic Compounds* (4th Edition) p. 254. Wiley (1956).

with conc. HCl and heated on a steam bath until the oily precipitate solidified (1,1′,3′,1″-dispirotriphthalane-3,3″-dione, VII, 2·9 g), m.p. 301–302° after crystallization from Ac_2O. (Lit.[4] m.p. 302–303°). (Found: C, 74·41; H, 3·55. Calc. for $C_{22}H_{12}O_5$: C, 74·15; H, 3·39%.)

o-*Di-(3-phthalidyl)benzene* (VIII). Following Clar's method,[4] from 2·0 g VII, 1·4 g VIII was obtained, m.p. 211–213° after crystallization from AcOH. (Lit.[4] m.p. 211–212°). (Found: C, 77·49; H, 4·43. Calc. for $C_{22}H_{14}O_4$: C, 77·18; H, 4·12%.)

Treatment of VIII *with* HI *and red* P. A mixture of VIII (1·3 g), red P (0·6 g), 55% HI (6 ml) and xylene (6 ml) was refluxed for 23 hr. The cooled reaction mixture was then worked up as described by Clar[4] to yield *o*-di(*o*-carboxybenzyl)benzene (IX, 1·0 g), m.p. 244–245° after crystallization from AcOH. (Lit.[4] m.p. 242–243°). (Found: C, 76·12; H, 5·39. Calc. for $C_{22}H_{18}O_4$: C, 76·28; H, 5·24%.)

The xylene layer afforded on concentration 30 mg pentaphene (X) as yellow plates, m.p. 253–256°. (Lit.[4] m.p. 256–257°); UV: 226, 245, 257, 390, 301, 315, 329, 345, 356 mμ, logϵ 4·79, 4·81, 4·91, 4·34, 4·73, 4·93, 4·53, 4·42, 4·25. (Found: C, 94·64; H, 5·21. Calc. for $C_{22}H_{14}$: C, 94·93; H, 5·07%.) MS shows a strong molecular peak at m/e 278.

Treatment of III *with* $KMnO_4$ *in water*. A mixture of finely ground III (1·0 g), $KMnO_4$ (2·0 g) and 0·5N NaOH (75 ml) was refluxed for 23 hr. The ppt was triturated with hot 2N H_2SO_4 containing some $NaHSO_3$. The light yellow insoluble solid (0·6 g) was identified as anthraquinone.

The basic filtrate was treated with MeOH, filtered, acidified with HCl and heated for 15 min on a steam bath. The ppt (VIII, 0·15 g) was filtered off and the filtrate was evaporated to dryness. The solid residue was sublimed and the sublimate dissolved in chf. Evaporation of the filtered soln gave a residue (0.3 g) which was identified as phthalic anhydride.

Treatment of dibenz[a,e]*tropone with aq* $KMnO_4$. A mixture of dibenz [*a,e*]tropone[10] (0·5 g), $KMnO_4$ (0·5 g) and 0·5N NaOH (25 ml) was refluxed for 3 hr. After addition of $NaHSO_3$ and acidification, an insoluble yellow solid (0·35 g) separated which was identified as anthraquinone.

Treatment of 5-hydroxy-6-benyldibenz[a,e]*tropone with aq* $KMnO_4$. A mixture of 5-hydroxy-6-phenyldibenz[a,e]tropone[8] (0·5 g), $KMnO_4$ (0·5 g) and 0·5N NaOH (50 ml) was refluxed for 1 hr. After addition of MeOH the ppt was collected and the MnO_2 eliminated in the usual way: 0·2 g of anthraquinone, m.p. 280–285° (sub.) was thus obtained. Acidification of the basic filtrate with HCl precipitated 2-benzoylbenzophenone-2′-carboxylic acid (50 mg), m.p. 222–225°.[8] The filtered soln was extracted with ethyl ether and the extract was evaporated to yield a residue (80 mg) which, after crystallization from pet. ether, was identified as benzoic acid. The same results were obtained in the analogous oxidation of 11-phenyl-10,11-dihydro-5H-dibenz[*a,d*]cycloheptene-5,10-dione.[11]

Acknowledgements—The authors wish to thank Dr. A. Mandelbaum (Technion, Israel Institute of Technology, Haifa) for the determination of the molecular mass of pentaphene, and Prof. G. Berti for full discussion of these results.

[10] G. Berti, *Gazz. Chim. Ital.* **87**, 293 (1957).

[11] J. W. Cook, *J. Chem. Soc.* 2160 (1926).