

A RING ENLARGEMENT IN THE 9,10-DIHYDROANTHRACENE SERIES

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Abstract—The carbinol II obtained from benzylideneanthrone (I) and benzylmagnesium chloride is dehydrated by acetic anhydride to 9,10-dibenzylidene-9,10-dihydroanthracene (III) and by a mixture of *p*-toluenesulphonic and formic acids to 1-benzylidene-4-phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (IV). A series of analogs of III have been prepared analogously. The mechanistic implications of the ring enlargement are discussed.

WHEN benzylideneanthrone (I) is treated with benzylmagnesium chloride, a tertiary carbinol (II) is obtained;¹ it shows hydroxyl absorption at 3300 cm⁻¹. The structure of II appears to be proven by the observations that its dehydration with boiling acetic anhydride leads to 9,10-dibenzylidene-9,10-dihydroanthracene (III). In fact, this is perhaps the simplest method to prepare III, which has been made before² by bromination and dehydrobromination of the not easily accessible^{2,3} 9,10-dibenzylanthracene. A series of substitution products of III has been prepared analogously. They are described in the Experimental section (Table 2).

When the dehydration of II was carried out with a mixture of formic and *p*-toluenesulphonic acids, an isomeric hydrocarbon was obtained. Its UV spectrum [246 (log 4.37); 310 m μ (4.10)] pointed to the formula of 1-benzylidene-4-phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (IV) [UV spectrum of 1-benzylidene-2,3,6,7-dibenzocyclohepta-2,4,6-triene: 4228 (4.62); 284 m μ (4.40)]. The formula of IV was established by oxidation to (benzoic acid and) the known 2-benzoyl-2'-carboxybenzophenone (V) and furthermore by an unambiguous synthesis.

4-Phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (VI) was oxidized with selenium dioxide⁵ to the corresponding ketone VII and the latter treated with benzylmagnesium chloride; the carbinol formed was dehydrated. The hydrocarbon so obtained was identical with that formed from II.

The structure of ketone VII was proven by an alternative pathway. It was hydrogenated to 4-phenyl-2,3,6,7-dibenzocyclohepta-2,6-dien-1-one (VIII). The latter was synthesized as follows: Benzhydrylidene-phthalide (IX)^{6,7} was reduced by means of

¹ For other reactions of I and methyleneanthrone with Grignard reagents, see P. L. Julian and A. Magnani, *J. Amer. Chem. Soc.* **56**, 2174 (1934); P. L. Julian, W. Cole and R. Schroeder, *Ibid.* **71**, 2368 (1949); P. L. Julian and W. J. Gist, *Ibid.* **57**, 2030 (1935).

² E. Bergmann and S. Fujise, *Liebigs Ann.* **480**, 188 (1930).

³ E. Lippmann and J. Pollak, *Monatsh.* **23**, 672 (1902).

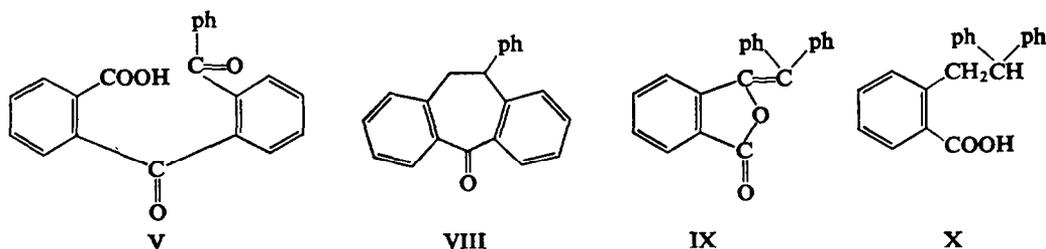
⁴ E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. Soc. Chim. Fr.* **18**, 684 (1951).

⁵ Method of Y. Amiel and D. Ginsburg, *Tetrahedron* **1**, 21 (1957).

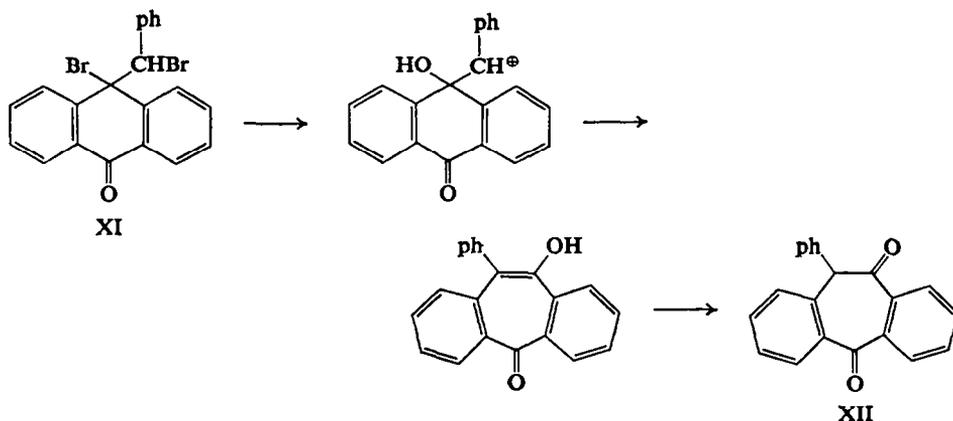
⁶ T. W. Koenig and J. C. Martin, *J. Org. Chem.* **29**, 1520 (1964).

⁷ J. Rigaudy and P. Derible, *Bull. Soc. Chim. Fr.* 3047 (1965).

phosphorus and hydriodic acid to *o*-(β,β -diphenylethyl) benzoic acid (X) and the latter cyclodehydrated with hydrofluoric acid, yielding the identical ketone (VIII). The



rearrangement of II to IV recalls the observation of Cook⁸ that treatment of the dibromide XI of benzylideneanthrone (I) with moist silver oxide gives 5-phenyl-2,3,6,7-dibenzocyclohepta-2,6-dien-1,4-dione (XII), a reaction which has to be formulated as follows:



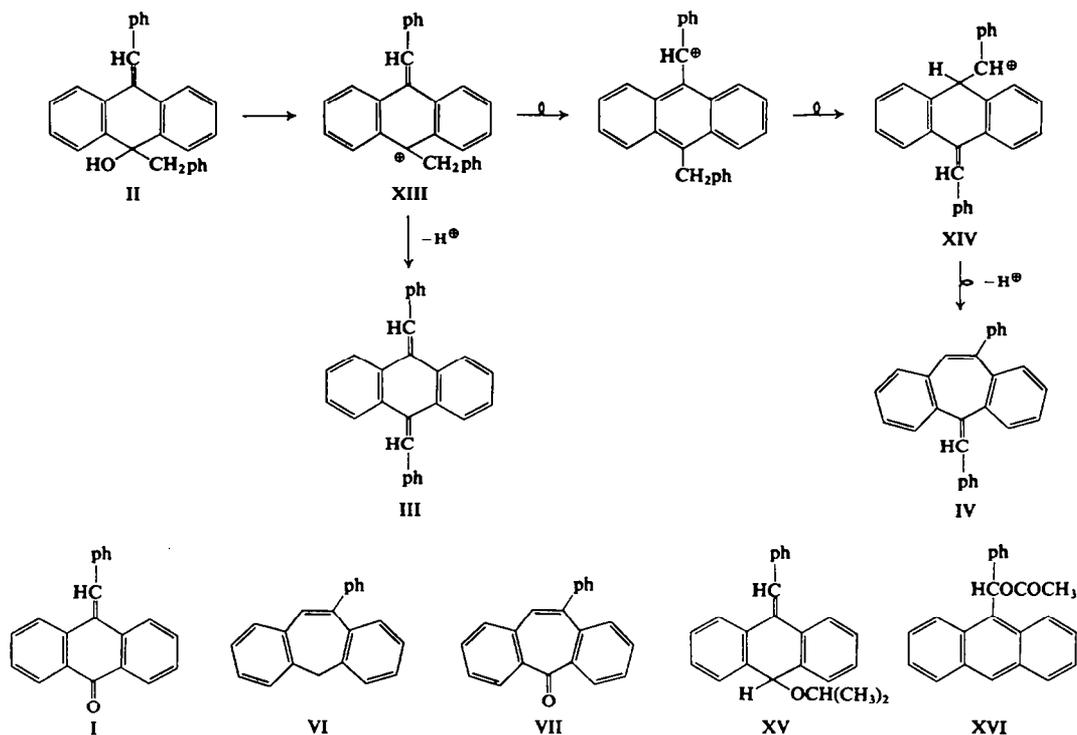
We have observed that the dibromide of 9-(*p*-chlorobenzylidene) anthrone behaves analogously, leading to the *p*-chlorophenyl analog of XII.

The mechanism of the observed ring enlargement is by no means obvious. It is unlikely that the carbonium ion (XIII) derived from II will undergo a rearrangement of the Wagner-Meerwein type; it is more in keeping with experience that IV is formed from a carbonium ion of formula XIV. Such rearrangements as XIII→XIV are not uncommon; apart from the now classical papers of Julian *et al.*, the observation⁹ may be cited that treatment of 9-benzylidene-10-isopropoxy-9,10-dihydroanthracene (XV) rearranges under the influence of acetic acid to 9-(α -acetoxybenzyl)-anthracene (XVI). The observed rearrangement can be rationalized as follows:

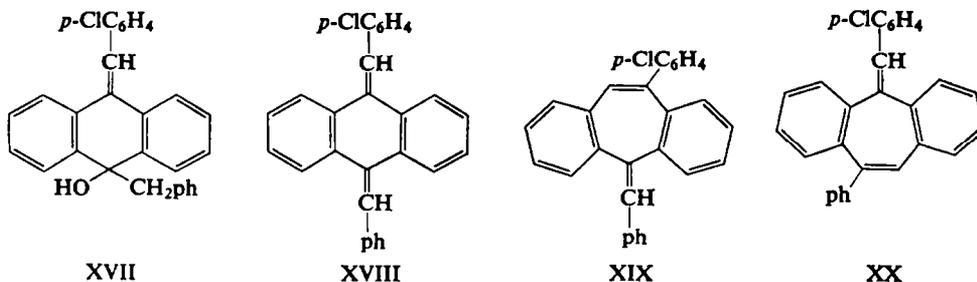
The benzylidene group appearing in IV is thus not the one present in the starting material II, but is derived from the Grignard reagent. The obvious consequences of this hypothesis are now being investigated. For instance, 9-(*p*-chlorobenzylidene)-10-

⁸ J. W. Cook, *J. Chem. Soc.* 58 (1928).

⁹ K. G. Flynn and G. Bergson, *Acta Chem. Scand.* 19, 756 (1965).



benzyl-9,10-dihydro-10-anthranol (XVII) gives on dehydration either 9-(*p*-chlorobenzylidene)-10-benzylidene-9,10-dihydroanthracene (XVIII), or an isomer which—if the above mechanism is correct—should be XIX and not XX



EXPERIMENTAL

9-Benzylideneanthrone (I)

The known methods^{10, 11} were improved as follows: A mixture of 50 g anthrone, 150 ml pyridine, 5 ml piperidine and 30 g benzaldehyde was refluxed for 6 hr. The solvents were evaporated *in vacuo* and the semisolid residue taken up in hot butanol. Upon cooling, the product crystallized. It was filtered and washed with MeOH. The lemon-yellow needles melted at 127°; yield, 56 g. (70%).

¹⁰ J. W. Cook, *J. Chem. Soc.* 2160 (1926).

¹¹ A. Haller and R. Padova, *C.R., Acad. Sci. Paris* 141, 859 (1905).

9-Benzylidene-10-benzyl-9,10-dihydro-10-anthranol (II)

In an atm of dry H, a Grignard soln was prepared from 4.8 g Mg and 24 g benzyl chloride in 250 ml ether. After addition of 200 ml more ether, 28 g powdered benzylideneanthrone was added slowly. When the exothermic reaction had subsided, the mixture was refluxed gently for 8 hr and decomposed with NH_4Cl aq. The ethereal soln left an oily residue which was triturated with MeOH. The product was a colourless solid (14 g; 38%) m.p. 127°; the mixture with benzylideneanthrone (m.p. 127°) gave a marked depression of the m.p. (Found: C, 89.6; H, 5.7. Calc. for $\text{C}_{28}\text{H}_{22}\text{O}$: C, 89.9; H, 5.9%).

9,10-Dibenzylidene-9,10-dihydroanthracene (III)

A soln of 3 g II in 50 ml Ac_2O was refluxed for 6 hr. Although on cooling some of the product crystallized, the product is best isolated by evapn *in vacuo* to dryness and recrystallization of the residue from xylene or butanol, yield, 2 g (63%); m.p. and mixed m.p. with an authentic sample⁷ 203–204°. Also the UV spectra ($\lambda_{\text{max}}^{\text{EtOH}}$ 220 (4.78); 250* (4.38); 380 $\text{m}\mu$ (4.35)) were identical. (Found: C, 93.9; H, 5.9. Calc. for $\text{C}_{28}\text{H}_{20}$: C, 94.3; H, 5.7%).

The substituted benzylideneanthrones were obtained by the method of Cook.¹⁰

9-(p-Chlorobenzylidene)anthrone; from butanol, m.p. 162°; yield 83%. (Found: C, 79.4; H, 4.2. Calc. for $\text{C}_{21}\text{H}_{13}\text{ClO}$: C, 79.6; H, 4.1%).

9-(o-Methoxybenzylidene)anthrone, from butanol, m.p. 153°; yield, 75%. (Found: C, 84.3; H, 5.3. Calc. for $\text{C}_{22}\text{H}_{16}\text{O}_2$: C, 84.6; H, 5.2%).

9-(o-Chlorobenzylidene)anthrone, from butanol, m.p. 115°; yield, 57%. (Found: C, 79.7; H, 4.5. Calc. for $\text{C}_{21}\text{H}_{13}\text{ClO}$: C, 79.6; H, 4.1%).

9-(p-Methylbenzylidene)anthrone, from butanol, m.p. 152°; yield, 77%. (Found: C, 88.9; H, 5.5. Calc. for $\text{C}_{22}\text{H}_{16}\text{O}$: C, 89.2; H, 5.4%).

9-(α -Naphthylmethylene)anthrone, from butanol, m.p. 141°; yield, 50%. (Found: C, 90.4; H, 5.1. Calc. for $\text{C}_{25}\text{H}_{16}\text{O}$: C, 90.4; H, 4.8%).

The reaction of these benzylideneanthrones with benzylmagnesium chloride was carried out as described for the unsubstituted benzylideneanthrone. The compounds formed are described in Table I.

The tertiary alcohols were dehydrated with boiling Ac_2O as described for the prep of II. The substitution products of II are described in Table 2.

The 9,10-di(arylmethylene)-9,10-dihydroanthracenes (Table 2) could theoretically exist in geometric isomers, but the sharpness of the m.p. and of the spots obtained by TLC show that the products are sterically homogeneous. However, their configuration has not yet been determined. Incidentally, it was observed that in the adsorbed state the products are somewhat sensitive to autoxidation; small quantities of anthraquinone are formed when the compounds are chromatographed on alumina.

Also the NMR spectra of two of the products which have been studied, confirm the structures of the di(arylmethylene)-9,10-dihydroanthracenes. In 9-(*p*-chlorobenzylidene)-10-benzylidene-9,10-dihydroanthracene (XVIII) two absorptions were observed, of the aromatic H atoms (17) at $\tau = 2.08\text{--}2.30$ and of the vinyl H atoms (2) at $\tau = 2.50\text{--}3.20$. Also in the corresponding *o*-methoxy-compound these two absorptions were found at $\tau = 2.0\text{--}2.3$ (17), and $\tau = 2.5\text{--}3.2$ (2), in addition to the absorption of the 3 H atoms of the methoxy groups at $\tau = 6.17$.

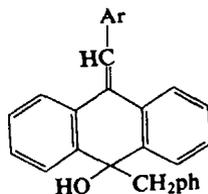
1-Benzylidene-4-phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (IV)

A mixture of 3 g II, 50 ml 95% formic acid and 3 g *p*-toluenesulphonic acid was refluxed for 8 hr in a N atm. The formic acid was distilled off, the residue poured into 10% NaOH aq and the mass extracted with benzene. Chromatography of the benzene soln on alumina gave a yellowish product of m.p. 155° (from butanol) in 1.5 g yield (50%). Renewed chromatography of a soln in benzene-pet. ether (1:5) removed a small amount of impurity; the yellow band first passing the column gave 1 g of the pure product, m.p. 145° (after recrystallization from butanol). (Found: C, 93.9; H, 6.0. Calc. for $\text{C}_{28}\text{H}_{20}$: C, 94.3; H, 5.7%).

2-Benzoyl-2'-carboxybenzophenone

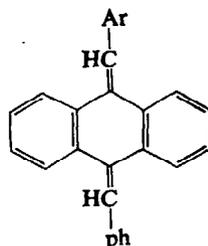
A current of O_3 was passed during 30 min through a suspension of 0.5 g IV in 25 ml glacial AcOH. The reaction product was diluted with water and evaporated to dryness *in vacuo*. The residue was treated with water for 30 min and again brought to dryness *in vacuo*. The product so obtained was

TABLE I 9 ARYLMETHYLENE-10-BENZYL-9,10-DIHYDRO-10-ANTHRANOLS



Ar	Product				Analysis			
	Recryst. from	M.p.°	Yield (%)	Formula	C, calc.	H, calc.	C, fd.	H, fd.
<i>p</i> -Chlorophenyl (XVII)	butanol	197	62	C ₂₈ H ₂₁ ClO	82.4	5.2	82.6	5.3
<i>o</i> -Methoxyphenyl	butanol	175	62	C ₂₉ H ₂₄ O ₂	86.2	5.9	86.0	5.9
<i>o</i> -Chlorophenyl	methanol	141	39	C ₂₈ H ₂₁ ClO	82.4	5.2	82.2	4.9
<i>p</i> -Tolyl	butanol	178	31	C ₂₉ H ₂₄ O	89.7	6.1	89.5	6.0
α -Naphthyl	butanol or methanol	193	40	C ₃₂ H ₂₄ O	90.7	5.4	90.8	5.8

TABLE 2. 9-ARYLMETHYLENE-10-BENZYLIDENE-9,10-DIHYDROANTHRACENES



Ar	Product				Analysis				UV Spectrum max $m\mu$ (log)	R_f (Al_2O_3 , benzene- pet. ether) 1:2
	Recryst. from	M.p.°	Yield (%)	Formula	C, calc.	H, calc.	C, fd.	H, fd.		
<i>p</i> -Chlorophenyl (XVIII)	butanol	178	10	$C_{28}H_{19}Cl$	86.1	4.9	86.3	4.9	250 (4.35), 330 (4.40) (EtOH); 340 (4.40) ($CHCl_3$)	0.85
<i>o</i> -Methoxyphenyl	butanol	156	12	$C_{29}H_{22}O$	90.2	5.7	89.9	5.8	345 (4.36) ($CHCl_3$)	0.81
<i>o</i> -Chlorophenyl	butanol	116-118	75	$C_{28}H_{19}Cl$	86.1	4.9	85.9	4.5	220 (4.45), 242 (4.32); 330 (4.40) (EtOH)	0.85
<i>p</i> -Tolyl	butanol	148	28	$C_{29}H_{22}$	94.0	6.0	93.8	5.9	233 (4.76); 247 (4.28); 334 (4.40) (EtOH)	—
α -Naphthyl	methanol	127	41	$C_{32}H_{22}$	94.5	5.5	94.2	5.4	220 (4.94); 335 (4.38) (EtOH)	—

dissolved in 20% NaOH aq and pptd with acid; its m.p. (210°) was raised by recrystallization from xylene to 215°. The lit¹² gives for the above compound m.p. 220°.

4-Phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-trien-1-one (VII)

To a well agitated, boiling soln of 0.7 g VI¹³ in 250 ml diglyme, 0.6 freshly sublimed SeO₂ was added over a period of 10 hr. The mixture was refluxed for 12 more hr and the solvent evaporated *in vacuo* and replaced by 50 ml EtOH, containing a little (1 ml) glacial AcOH. After addition of 0.2 g of Zn dust, the soln was refluxed for 30 min and evaporated *in vacuo* to dryness. The residue was taken up with water and extracted 4 times with 50 ml CH₂Cl₂. The dried soln was evaporated and the product dissolved in benzene and chromatographed on alumina. Thus, 0.1 g VI and 0.6 g (87%) VII were obtained. The ketone melted at 118°. $\lambda_{\max}^{\text{EtOH}}$ 258 (4.49); 312 (4.04); 345^a m μ (3.60), ν_{\max}^{KBr} 1680 cm⁻¹ (C=O). (Found: C, 89.6; H, 4.9. Calc. for C₂₁H₁₄O; C, 89.4; H, 5.0%).

1-Benzyl-4-phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-trien-1-ol.

A soln of 0.7 g VII in 30 ml ether was added to a Grignard soln, prepared from 0.12 g Mg and 0.5 g benzyl chloride. After addition of 50 ml benzene, the mixture was refluxed for 5 hr and decomposed with ice and NH₄Cl. The colourless product (800 mg; 89%) melted at 178°, ν_{\max}^{KBr} 3500 cm⁻¹ (OH); no carbonyl absorption. (Found: C, 89.8; H, 6.0. Calc. for C₂₈H₂₂O; C, 89.8; H, 5.8%).

1-Benzylidene-4-phenyl-2,3,6,7-dibenzocyclohepta-2,4,6-triene (IV)

The foregoing compound (800 mg) was refluxed for 4 hr with 50 ml Ac₂O, containing a few drops of conc. H₂SO₄. The soln was concentrated and the residue treated with water and NaHCO₃ and extracted with benzene, CH₂Cl₂ and again with benzene. The evapn of the united extracts gave an oil which crystallized upon treatment with butanol. Repeated recrystallization from the same solvent gave the hydrocarbon of m.p. 140° (yield, 20%). Admixture of the product obtained from II (see p. 144) did not lower the m.p. Also on TLC on celite, identical spots were obtained (*R_F* 0.41 and 0.42; eluent: benzene-pet. ether (2:1)) and the IR spectra were fully superimposable.

o-(β,β -Diphenylethyl) benzoic acid (X)

A mixture of 15 g IX,^{6,7} 13 g red P and 65 ml 68% HI was refluxed, with stirring, for 32 hr, cooled, filtered and the solid phase washed with a little water. It was then heated with ammonia soln and the soln filtered and acidified. The acid (yield, quant.) was recrystallized from cyclohexane and melted at 152°. (Found: C, 83.6; H, 5.9. Calc. for C₂₁H₁₈O₂; C, 83.4; H, 6.0%).

4-Phenyl-2,3,6,7-dibenzocyclohepta-2,6-dien-1-one (VIII)

(a) A mixture of 3.5 g X and 50 ml anhyd HF was kept at room temp for 24 hr and brought to dryness. The product was twice triturated with water and then extracted with 3 portions of 50 ml CH₂Cl₂. The extract was washed with NaHCO₃ aq, dried and evaporated and the residue purified by vacuum distillation; b.p. 215–220° (0.2 mm); yield, 2.0 g (62%). $\lambda_{\max}^{\text{EtOH}}$ 252 (4.14); 290^a m μ (3.36). ν_{\max}^{KBr} 1670 cm⁻¹. (Found: C, 89.0; H, 5.7. Calc. for C₂₁H₁₆O; C, 88.7; H, 5.6%).

(b) A soln of 100 mg VII in 25 ml glacial AcOH was hydrogenated, using Pt as catalyst. The filtered soln was evaporated; the yellowish, oily residue gave the same IR spectrum as the product obtained sub (a).

9-Bromo-9-(α -bromo-*p*-chlorobenzyl)-10-anthrone

To a suspension of 13 g 9-(*p*-chlorobenzylidene) anthrone (see p. 144) in 200 ml CCl₄, 6.8 g Br was added. The soln so obtained was filtered and brought to dryness *in vacuo* and the residue dissolved in toluene and pptd with pet. ether (100–120°). Thus a yellowish crystalline powder was obtained (14 g; 70%) which melted at 163°. (Found: C, 52.9; H, 3.0. Calc. for C₂₁H₁₃Br₂ClO; C, 52.9; H, 2.7%).

¹² A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.* **73**, 1673 (1951).

¹³ J. Rigaudy and P. Tardieu, *C.R. Acad. Sci. Paris* **244**, 2939 (1957), P. Tardieu, *Ann. Chim.* [13], **6**, 1445 (1961).

5-(p-Chlorophenyl)-2,3,6,7-dibenzocyclohepta-2,6-diene-1,4-dione

To a soln of 10 g of the foregoing product in 150 ml acetone, 10 g Ag_2O and 1 ml water were added, and the mixture was refluxed with stirring for 3 hr, filtered and brought to dryness *in vacuo*. The product (5.8 g; 80%) was recrystallized from EtOH and melted at 156° . It contained Cl, but no Br. $\lambda_{\text{max}}^{\text{CHCl}_3}$ 275 (4.18); 310 (3.78); 375 $\text{m}\mu$ (2.45). $\nu_{\text{max}}^{\text{KBr}}$ 1680 cm^{-1} (Found: C, 75.4; H, 3.8. Calc. for $\text{C}_{21}\text{H}_{13}\text{ClO}_2$: C, 75.3; H, 3.9%).

9-(p-Chlorobenzylidene) 10-benzyl-9,10-dihydro-10-anthranol

In small portions, 15.8 g 9-(*p*-chlorobenzylidene)anthrone (see p. 144) was added at room temp and in an inert atmosphere to a soln, prepared from 1.7 g of Mg and 7.6 g benzyl chloride in 300 ml ether. The reaction mixture was refluxed for 3 hr and decomposed with cold NH_4Cl aq. Evapn of the ethereal soln *in vacuo* gave a semisolid product which was triturated with MeOH and recrystallized from butanol, as white needles of m.p. 197° ; yield, 10 g (45%). (Found: C, 82.8; H, 5.3. Calc. for $\text{C}_{28}\text{H}_{21}\text{ClO}$: C, 82.2; H, 5.2%).

Rearrangement. A suspension of 5 g of the foregoing compound in 50 ml 95% formic acid was refluxed with 3 g *p*-toluenesulfonic acid (hydrate) for 6 hr. The excess formic acid was evaporated *in vacuo* and the residue treated with 10% Na_2CO_3 aq and taken up with benzene. The residue was dissolved in butanol, from which the product crystallized (4.5 g; 93%) in yellowish crystals of m.p. 168° . Chromatography of the benzene solution of the product on alumina did not change the m.p. $\lambda_{\text{max}}^{\text{EtOH}}$ 245 (4.28); 315 $\text{m}\mu$ (4.00). (Found: C, 86.4; H, 5.3. Calc. for $\text{C}_{18}\text{H}_{19}\text{Cl}$: C, 86.2; H, 4.9%).