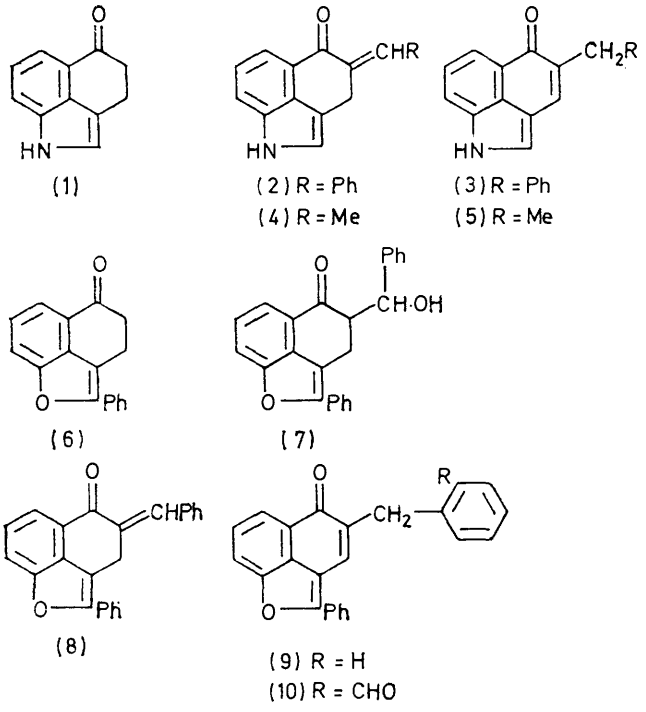
Quinone Methides derived from Uhlé's Ketone

By Gavin M. Buchan and Alan B. Turner,* Chemistry Department, University of Aberdeen, Aberdeen AB9 2UE, Scotland

Base-catalysed condensation of 3,4-dihydrobenz[*cd*]indol-5(1*H*)-one (1) with aromatic aldehydes gives 4-arylmethylene-3,4-dihydrobenz[*cd*]indol-5(1*H*)-ones (11) and 4-benzylbenz[*cd*]indol-5(1*H*)-ones (12); the former are converted into the latter by acid. Spectroscopic studies indicate that the latter compounds exist, in solution, as the uncharged quinone methides, rather than as the aromatic zwitterion forms.

CONDENSATION of 3,4-dihydrobenz[*cd*]indol-5(1*H*)-one (1) (Uhle's ketone) with benzaldehyde in the presence of alkali is reported [1] to give the benzylidene derivative (2), although no evidence was offered in support of this structure rather than the tautomeric quinone methide form (3). The reported spectroscopic properties of the compound are compatible with either structure; in the n.m.r. spectrum the broad two-proton singlet could be attributed either to the doubly allylic methylene group in (2) or to the benzylic methylene group in (3).

The analogous condensation of Uhlé's ketone (1) with acetaldehyde was attempted, as the products (4) and (5) would be readily distinguishable by n.m.r. However, only an intractable mixture was obtained even



(1)
(2) R = Ph
(4) R = Me
(3) R = Ph
(5) R = Me
(6)
(7)
(8)
(9) R = H
(10) R = CHO

after acetylation, and no better result was achieved with formaldehyde. Attempts to prepare the hydroxymethylene derivative (or the hydroxymethyl derivative) by condensation with ethyl formate in the presence of sodium hydride or sodium ethoxide gave only unchanged starting material, in marked contrast to the behaviour of α-tetralone, which forms 2-hydroxymethylene-1-tetralone in good yield by both methods.[2,3]

The behaviour of the naphthofuran (6) towards benzaldehyde provided some guidance, as the benzyl alcohol (7) was formed in the presence of triethylamine.[4] The alcohol (7) was dehydrated to the benzylidene derivative (8) with toluene-*p*-sulphonyl chloride in pyridine. Alternatively, product (8) could be obtained directly from the ketone (6) by condensation with benzaldehyde in an acetic acid–sulphuric acid. Further treatment of the benzylidene derivative (8) with triethylamine resulted in rearrangement to the quinone methide (9).[5]

Analogous transformations could not be carried out on Uhlé's ketone, since no reaction was observed on treatment of the ketone with benzaldehyde in triethylamine, and the attempted condensation in acetic acid–sulphuric acid led only to decomposition. However, it was possible to compare the spectral data for the adduct (2)/(3) with those recorded for compounds (8)—(10) (Table 1). The n.m.r. data favoured the

TABLE 1

Spectral data of benzaldehyde condensation products

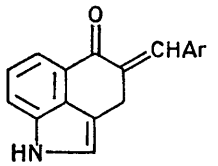
Compound	ν_{CO}/cm^{-1}	τ(CH$_2$)	$\lambda_{max.}$/nm
(2)/(3)	1 650	5.66 (s)	230, 298, 414
(8)	1 665	5.57 (d)	300, 385
(9)	1 643	6.02 (s)	
(10)	1 635	5.57 (s)	250, 400

quinone methide structure (3), since the signal for the methylene group appeared as a singlet, as opposed to the doublet observed for the methylene group in the benzylidene derivative (8); the i.r. and u.v. data provided no clear evidence for either structure.

Reactions of Uhlé's ketone (1) with a series of substituted aromatic aldehydes were then carried out in the presence of potassium hydroxide as before, and in most cases the product was precipitated in reasonable yield as orange crystals. With some aldehydes, however, the yield was vanishingly small, and so work-up involved evaporation of the solution, partition of the residue between ethyl acetate and water, and preparative t.l.c. of the organic extract. By this means, there was obtained a second series of products, which were shown to be isomeric with the first series by mass spectrometry, but which differed considerably in other spectral

[1] C. A. Grob and P. Payot, *Helv.*, 1953, **36**, 839.
[2] F. L. Weisenborn, D. C. Remy, and T. L. Jacobs, *J. Amer. Chem. Soc.*, 1954, **76**, 552.
[3] C. Ainsworth, *Org. Synth.*, Coll. Vol. IV, 1963, p. 536.
[4] D. H. R. Barton, B. Halpen, Q. N. Porter, and D. J. Collins, *J. Chem. Soc.* (*C*), 1971, 2166.
[5] E. Aufderhaar, J. E. Baldwin, D. H. R. Barton, D. J. Faulkner, and M. Slaytor, *J. Chem. Soc.* (*C*), 1971, 2175.

properties. For convenience, these two sets of products are designated types A and B, respectively, and their members are listed in Tables 2 and 3, together with relevant spectral data.



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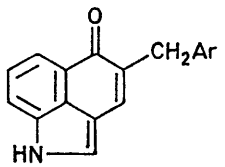


(12)

TABLE 2

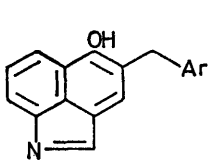
Spectral data of type A products (11)

Ar	$\tau(CH_2)$	$\nu_{max.}/cm^{-1}$	$\lambda_{max.}/nm$	log ε
Ph		3 260	230	4.31
	5.66	1 650	298	4.14
		1 625	414	3.83
		3 280	247	4.20
3,4-$(CH_2O_2)C_6H_3$	5.66	1 645	345	4.05
		1 620	418	3.92
		3 270	249	4.14
4-MeO·C_6H_4	5.68	1 650	336	4.13
		1 630	418	3.95
		3 260	249	4.01
2-MeO·C_6H_4	5.78	1 660	333	3.79
		1 630	416	3.77
		3 380	247	4.28
4-$(PhCH_2O)C_6H_4$	5.65	1 660	336	4.24
		1 630	415	4.01

Type A products are characterised by a two-proton n.m.r. singlet at τ 5.7, a fairly simple u.v. spectrum, a sharp N–H stretching i.r. band at 3 270 cm^{-1} (also present in the spectrum of Uhlé's ketone), and a strong carbonyl band in the range 1 660—1 645 cm^{-1}.

Type B products are characterised by a two-proton singlet at τ 6.2—6.4, a much more complex u.v. spectrum, and an i.r. spectrum showing broad absorption at about 3 400 cm^{-1} together with a triplet at 3 160—3 070 cm^{-1}, and a medium-intensity band at 1 640 cm^{-1} (this being the only absorption in the region 1 700—1 600 cm^{-1}). Furthermore, the u.v. spectra of type B products are altered significantly and consistently by the addition of dilute sodium hydroxide, the maxima at 275 and 420 nm being moved to longer wavelength by *ca.* 15 and 50 nm, respectively. The spectra of type A compounds remain unchanged upon addition of base.

At first, these findings suggested the fully unsaturated structure (13) for the type B products. It was then noted that dehydrogenation of Uhlé's ketone with palladium–charcoal [6] gave a product whose i.r. and u.v. spectra matched perfectly those of the type B compounds. Grob and Hofer [6] had formulated this product as the quinone methide (14; R = H) rather than the phenolic compound (15; R = H), an assignment which followed from the formation of the *N*-acetate (14; R = Ac) and the *N*-methyl derivative (14; R = Me) on treatment with acetic anhydride and dimethyl sulphate, respectively. The identification of



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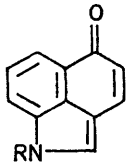

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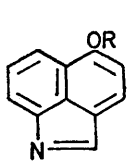


(15)

these compounds as the *N*-substituted quinone methide forms rather than the *O*-substituted isomers (15; R = Ac or Me) was based [6] upon the isolation of phenolic products upon partial hydrogenation. It was easily confirmed that (14; R = H) was the correct structure for the dehydrogenation product, as its ^{13}C n.m.r. spectrum showed a signal at 184 p.p.m. This is well beyond the range of any functional group apart from carbonyl,[7] and compares favourably with values of 198 and 187 p.p.m. for the carbonyl groups of the ketone (1) and its condensation product (2)/(3) with benzaldehyde. Further evidence was provided by dehydrogenation of the *N*-acetate of Uhlé's ketone

TABLE 3

Spectral data of type B products (12)

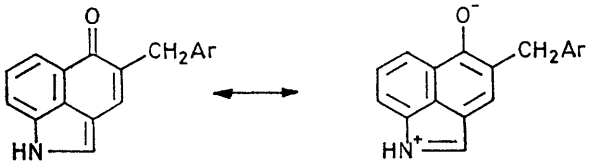
Ar	$\tau(CH_2)$	$\nu_{max.}/cm^{-1}$	$\lambda_{max.}/nm$	log ε	$\lambda_{max.}$(NaOH)/nm *
		3 400	220	4.39	220
		3 140	241	4.04	248
3,5-Br_2-4-$(PhCH_2O)C_6H_2$	6.40	3 110	276	3.96	288
		3 070	305sh	3.53	364
		1 640m	355	3.57	381
			416	4.06	472
		3 400	227	4.27	228
		3 160	275	4.09	248
4-$(PhCH_2O)C_6H_4$	6.17	3 120	304sh	3.72	288
		3 080	355	3.76	370
		1 640m	418	4.11	473
		3 410	247	3.97	250
		3 160	276	4.00	288
3,4-$(MeO)_2C_6H_3$	6.25	3 120	355	3.66	370
		3 080	420	4.04	475
		1 640m			

* Recorded in EtOH containing *ca.* 2% of 2N-NaOH; in this solution the quinone methide (14; R = H) had $\lambda_{max.}$ 251, 283, 360, 378, and 460 nm.

[6] C. A. Grob and B. Hofer, *Helv. Chim. Acta*, 1952, **35**, 2095.
[7] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Organic Chemistry Monographs, vol. 24, Academic Press, New York, 1972.

with palladium–charcoal, since both g.l.c. and t.l.c. of the product mixture revealed the presence of compound (14; R = Ac) obtained from the ketone (1) by dehydrogenation followed by acetylation.

With the quinone methide structure (14; R = H) established for the dehydrogenation product of Uhlé's ketone, it followed immediately from comparison of i.r. and u.v. spectra that the type B products had a similar quinone methide structure (12). The reason why these quinone methides exhibit medium-intensity rather than



(12a) (12b)

strong carbonyl absorption in their i.r. spectra is presumably their dipolar character [(12a) ⟷ (12b)], with a significant contribution from the zwitterionic form (12b). Quinone methides of type (9), which would not be expected to show such pronounced dipolar character, show strong carbonyl absorption at the same frequency as the nitrogen analogues. A number of quinone methides having dipolar character have been prepared in recent years.[8,9] These include both *ortho*-[10] and *para*-quinone methides,[11,12] and wide variation in the extent of zwitterion formation is apparent from their spectral properties, particularly amongst quinone cyclopropides and tropides.

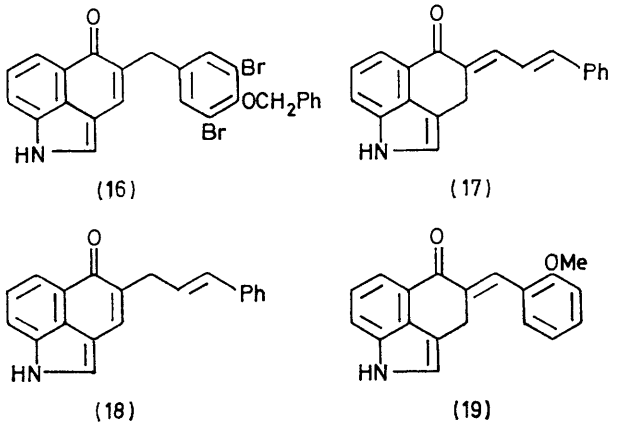
Apart from explaining the moderate carbonyl absorption, the zwitterion form (12b) could also be responsible for changes in the u.v. spectra observed upon addition of base. Systematic studies of the effect of solvent polarity upon u.v. spectra have been used by several workers (*e.g.* ref. 11) to differentiate the non-polar quinone methide structures from their zwitterion forms. Thus on increasing the solvent polarity, the non-polar quinone methides [structure (12a)] were expected to exhibit positive solvatochromism, whereas their dipolar forms (12b) should exhibit negative solvatochromism. The u.v. spectrum of the benzyloxy-compound (16) was determined in a number of solvents listed in order of increasing polarity on the E_T scale[13] in Table 4. Although the trend is not uniform, it is clear that the observed $\lambda_{max.}$ value is higher in the more polar solvents, indicating that the quinonoid structure predominates. Inherent in this argument in favour of structure (16) is the assumption that changing the solvent does not alter significantly the electron distribution in the ground state of the molecule in favour of the dipolar structure [≡(12b)]. Fortunately, apart from the shift in position of the band at the longest wavelength, the spectra recorded in acetonitrile, propan-2-ol, and ethanol were identical, which would have been unlikely had they been the spectra of distinct species. Thus structure (12a) was established for type B compounds in solution, although in the solid state their i.r. spectra (KBr discs) were more indicative of the ionic structure (12b). Unfortunately, attempts to record solution i.r. spectra for the series were thwarted by their poor solubility in the appropriate solvents.

With structure (12) established for type B products, there remained only the benzylidene structure (11) for the type A products. This was confirmed by the condensation of Uhlé's ketone (1) with cinnamaldehyde: the two possible products (17) and (18) were easily distinguishable on the basis of their n.m.r. data. The

TABLE 4

U.v. absorption of the quinone methide (16)

Solvent	$[CH_2]_4O$	Me_2CO	MeCN	Pr^iOH	EtOH	$HCO{\cdot}NH_2$
$\lambda_{max.}$/nm	402	401	401	410	416	417



(16) (17) (18) (19)

methylene group in the product (17) occupies a similar environment to those in the other arylmethylene compounds (11), the protons being chemically equivalent and subject only to allylic coupling, and therefore predicted to appear as a singlet in the n.m.r. spectrum, whereas the methylene group in the product (18), being coupled to the adjacent olefinic proton as well as allylically coupled, was expected to appear as a multiplet. In the event, the product which crystallised from the reaction mixture gave i.r. and u.v. spectra similar to

[8] *Cf.* R. Gompper and H.-U. Wagner in ' The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, New York, 1974, p. 1145.

[9] *Cf.* G. M. Buchan, Ph.D. Thesis, Aberdeen University, 1975, pp. 4—12.

[10] R. Gompper and R. R. Schmidt, *Z. Naturforsch.*, 1962, **176**, 851; R. Gompper and E. Kutter, *Chem. Ber.*, 1965, **98**, 1365; E. Klingsberg, *J. Org. Chem.*, 1972, **37**, 3226; R. Pinel, Y. Mollier, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 856; J. P. de Barbeyrac, D. Gonbeau, and G. Pfister-Guillouzo, *J. Mol. Structure.*, 1963, **16**, 103.

[11] R. Gompper, R. R. Schmidt, and E. Kutter, *Annalen*, 1965, **684**, 37; B. Föhlisch and P. Bürgle, *ibid.*, 1967, **701**, 67.

[12] S. J. Davidson and W. P. Jencks, *J. Amer. Chem. Soc.*, 1969, **91**, 225; H. G. Benson and S. N. Murrell, *J.C.S. Faraday II*, 1972, 137; S. Kumoi, H. Kobayashi, and K. Ueno, *Talanta*, 1972, **19**, 505; J. M. Hill, *J. Org. Chem.*, 1967, **32**, 3214; J. J. Looker, *ibid.*, p. 2941; D. L. Coffen and P. E. Garrett, *Tetrahedron Letters*, 1969, 2043; W. Broser and M. Brockt, *ibid.*, 1968, 5331; B. Föhlisch and D. Krockenberger, *Chem. Ber.*, 1968, **101**, 2717, 3990; K. Hirai, *Tetrahedron*, 1971, **27**, 4003; P. L. Pauson, G. R. Proctor, and R. Watson, *J. Chem. Soc.* (*C*), 1971, 2399.

[13] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

those of the other type A products, and showed a two-proton singlet at τ 5.6 in its n.m.r. spectrum, which was compatible only with structure (17). A second product, obtained in poor yield, had i.r. and u.v. spectra which matched those of type B compounds, and showed a multiplet at τ 6.5 in its n.m.r. spectrum consistent with structure (18).

It was possible to rearrange the arylmethylene compounds of type (11) to the quinone methides (12) by treatment with acid; an attempted demethylation of the methyl ether (19) in hot acetic acid–hydrobromic acid gave a crude product whose i.r. spectrum conformed to those of the quinone methides, and similar treatment of (2) gave a crude product having i.r. and u.v. spectra consistent with structure (3). The rearrangement was most clear-cut in the case of the cinnamylidene derivative (17). Its n.m.r. spectrum [solvent $(CD_3)_2SO$] showed the two-proton singlet at τ 5.66 characteristic of the allylic methylene group. However, when trifluoroacetic acid was added to the solution and the spectrum was re-run, this signal was replaced by a two-proton multiplet centred at τ 6.50, and the pattern of the aromatic/olefinic envelope was altered to match that observed for the quinone methide (18). The behaviour of the arylmethylene compounds (2) and (17) towards acid and base is the exact opposite of the behaviour displayed by the naphthofuran analogue (8) described by Barton.[4,5] Whereas the latter is stable under acid conditions, but rearranges to the quinone methide (9) with base, the arylmethylene derivatives of Uhlé's ketone are stable in base, but rearrange to the quinone methides in the presence of acid.

In keeping with their quinonoid structure, doubly charged ions accounted for an appreciable proportion of the ion current in the mass spectra of this series of compounds. In most cases the parent ion formed the base peak in the spectrum, and the M^{2+} ion was observed in all spectra except those of compounds containing the readily removed benzyloxy-group. The ionizing conditions were too harsh to allow distinction between type A and B compounds. In the mass spectrum of the quinone methide (14; R = H) the parent ion was also the base peak, and the M^{2+} ion was present together with other doubly charged fragments.

EXPERIMENTAL

I.r. spectra were recorded for KBr discs with a Perkin-Elmer 237 spectrophotometer, and u.v. spectra for ethanolic solutions with a Perkin-Elmer 137 instrument. N.m.r. spectra were determined for solutions in $(CD_3)_2SO$ (also used as internal standard) with a Varian HA-100 or Perkin-Elmer A-12A spectrometer, and mass spectra were recorded with an A.E.I. MS-30 spectrometer at 70 eV. Ions of $m/e > 70$ and of intensity $> 10\%$ are recorded together with important doubly-charged ions. G.l.c. was performed on 2 m × 3 mm (i.d.) columns packed with 1.5% fluorosilicone oil FS1265 on AW-DMCS Chromosorb W (80—100 mesh) at 200 °C with a nitrogen flow rate of 26 ml min^{-1} (Perkin-Elmer F-11 instrument). M.p.s were determined with a Kofler hot-stage apparatus.

Uhlé's ketone was supplied by Parke-Davis, Ltd. 4-Benzyloxybenzaldehyde and 4-benzyloxy-3,5-dibromobenzaldehyde were prepared by heating 4-hydroxybenzaldehyde and 3,5-dibromo-4-hydroxybenzaldehyde,[14] respectively, with benzyl chloride in acetone under reflux in the presence of anhydrous potassium carbonate.

Condensation of Uhlé's Ketone[15] *with Aromatic Aldehydes.*—*Type A products* (11) (cf. *ref.* 1). To a solution of the ketone (2 mmol) and the appropriate aldehyde (2 mmol) in the minimum amount of ethanol was added a solution of potassium hydroxide (200 mg) in aqueous ethanol (2 ml), and the mixture was left overnight at room temperature. The precipitated product was collected and recrystallised from ethanol or aqueous ethanol. The following compounds were obtained: 4-benzylidene-3,4-dihydrobenz[*cd*]indol-5(1*H*)-one (2) (49%), decomp. gradually above 185° (lit.,[1] m.p. 197—200°) (Found: M^+, 259.0996. Calc. for $C_{18}H_{13}NO$: *M*, 259.0997), *m/e* 259 (100%), 258 (50), 242 (27), 231 (18), 230 (65), 202 (19), and 154 (20); *m/2e* 129.5 (1) and 128.5 (8); 3,4-*dihydro*-4-(3,4-*methylenedioxybenzylidene*)*benz*[cd]*indol*-5-(1H)-*one* (49%), m.p. 213—214° (Found: C, 75.3; H, 4.4; N, 4.4%; M^+, 303.0893. $C_{19}H_{13}NO_3$ requires C, 75.3; H, 4.3; N, 4.6%; *M*, 303.0895), *m/e* 303 (100%), 302 (20), 286 (10), 275 (20), 274 (48), 244 (19), 217 (17), 189 (18), and 154 (25); *m/2e* 151.5 (1), 150.5 (2), and 136.5 (8); 3,4-*dihydro*-4-(4-*methoxybenzylidene*)*benz*[cd]*indol*-5(1H)-*one* (45%), m.p. 195—200° (Found: C, 78.7; H, 5.5; N, 5.0%; M^+, 289.1102. $C_{19}H_{15}NO_2$ requires C, 78.9; H, 5.2; N, 4.9%; *M*, 289.1102), *m/e* 289 (100%), 288 (11), 274 (15), 260 (17), and 246 (14); *m/2e* 144.5 (3) and 143.5 (2); 3,4-*dihydro*-4-(2-*methoxybenzylidene*)*benz*[cd]-*indol*-5(1H)-*one* (74%), m.p. 170—175° (Found: C, 77.5; H, 5.4; N, 4.6%; M^+, 289.1102), *m/e* 289 (49%), 274 (10), 258 (100), 246 (12), 244 (11), 189 (11), 183 (38), 182 (48), 171 (20), 170 (14), 154 (16), 143 (22), and 115 (20); *m/2e* 144.5 (0.5); 4-(4-*benzyloxybenzylidene*)-3,4-*dihydrobenz*[cd]-*indol*-5(1H)-*one* (46%), m.p. 162—165° (Found: C, 82.1; H, 5.5; N, 3.8%; M^+, 365.1414. $C_{25}H_{19}NO_2$ requires C, 82.2; H, 5.2; N, 3.8%; *M*, 365.1415), *m/e* 365 (20%), 275 (18), 274 (90), and 91 (100); 4-*cinnamylidene*-3,4-*dihydrobenz*[cd]-*indol*-5(1H)-*one* (17) (23%), m.p. 171—175° (Found: C, 84.1; H, 5.4; N, 4.9%; M^+, 285.1153. $C_{20}H_{15}NO$ requires C, 84.3; H, 5.3; N, 4.9%; *M*, 285.1153), *m/e* 285 (24%), 284 (10), 195 (12), and 194 (100); *m/2e* 142.5 (0.5) and 141.5 (2.5), $\nu_{max.}$ 3 250, 1 640, and 1 617 cm^{-1}, $\lambda_{max.}$ 250, 347, and 427 nm (log ε 4.15, 4.30, and 3.99).

Type B products (12). 4-(4-*Benzyloxy*-3,5-*dibromobenzyl*)-*benz*[cd]*indol*-5(1H)-*one* (16). Condensation of the ketone (1) (1 mmol) with an equimolar amount of 4-benzyloxy-3,5-dibromobenzaldehyde by the above method failed to elicit any precipitate. The mixture was evaporated *in vacuo* and the residue was partitioned between ethyl acetate (20 ml) and water (15 ml) containing 2N-hydrochloric acid (2 ml). The organic layer was separated, dried ($MgSO_4$), and evaporated to give a red solid (604 mg). Preparative t.l.c. on silica gel, developed in chloroform, gave a yellow solid (105 mg), which, on trituration with ether, gave the *quinone methide* (16) (45 mg, 9%) as a yellow powder, m.p. 257—258° (Found: M^+, 522.9605. $C_{25}H_{17}{}^{79}Br^{81}BrNO_2$ requires *M*, 522.9606), *m/e* 523 (4%), 435 (18), 434 (50), 432 (100), 431 (19), 430 (48), and 91 (100).

4-(4-*Benzyloxybenzyl*)*benz*[cd]*indol*-5(1H)-*one*. The

[14] C. Paal, *Ber.*, 1895, **28**, 2407.
[15] R. E. Bowman, T. G. Goodburn, and A. A. Reynolds, *J.C.S. Perkin I*, 1972, 1121.

mother liquor from the preparation of the above 4-benzyloxybenzylidene derivative on similar work-up gave a dark red solid (300 mg), which after repeated t.l.c. in chloroform gave the *quinone methide* (20 mg, 4%), m.p. 202—203° (Found: M^+, 365.1417. $C_{25}H_{19}NO_2$ requires M, 365.1415), *m/e* 365 (20%), 275 (25), 274 (100), and 91 (56).

4-(3,4-*Dimethoxybenzyl*)*benz*[cd]*indol*-5(1H)-*one*. Condensation of the ketone (1) (171 mg) with veratraldehyde (166 mg) failed to give a precipitate. The above work-up gave a yellow solid (111 mg) which, on trituration with benzene, yielded the *quinone methide* as a yellow powder (80 mg, 25%), m.p. 235—238° (Found: M^+, 319.1206. $C_{20}H_{17}NO_2$ requires M, 319.1208), *m/e* 319 (100%), 304 (32), 288 (18), 244 (11), and 182 (9); *m/2e* 159.5 (4), 143.5 (4), 136.5, 128.5, and 122.5 (all 5), and 103.5 (6).

Acetylation of this material (70 mg) by heating with acetic anhydride (1.5 ml) containing freshly fused sodium acetate (80 mg) on a steam-bath until a clear solution was obtained, followed by addition of ice–water (7.5 ml), gave the N-*acetate* as pale yellow plates (69 mg, 86%), m.p. 147—150° (Found: C, 72.9; H, 5.4; N, 3.7. $C_{22}H_{19}NO_4$ requires C, 73.2; H, 5.3; N, 3.9%), $\lambda_{max.}$ 243, 269, and 369 nm (log ε 4.17, 4.13, and 4.18), $\nu_{max.}$ 1 730, 1 650, 1 635, and 1 610 cm^{-1}.

4-*Cinnamylbenz*[cd]*indol*-5(1H)-*one*. The mother liquor from the preparation of the cinnamylidene derivative (17), treated as above, gave a red glass (60 mg) which on further t.l.c. gave the *cinnamyl derivative* (18) (35 mg) as a yellow amorphous solid, m.p. 195—200° (decomp. above 180°) (Found: M^+, 285.1151. $C_{20}H_{15}NO$ requires M, 285.1153), $\lambda_{max.}$ 255, 273, 360, and 419 nm (log ε 4.25, 4.16, 3.68, and 4.02), changed upon addition of 2N-NaOH to $\lambda_{max.}$ 290 and 480 nm, $\nu_{max.}$ 3 410, 3 150, 3 110, 3 070, and 1 640 cm^{-1}, *m/e* 285 (8%), 195 (11), and 194 (100); *m/2e* 142.5 (0.2) and 141.5 (0.6).

Benz[cd]*indol*-5(1H)-*one* [1] (14; R = H). This exhibited *m/e* 169 (100%), 141 (22), 140 (10), and 114 (15); *m/2e* 84.5 (1) and 70.5 (4).

Dehydrogenation of 1-*Acetyl*-3,4-*dihydrobenz*[cd]*indol*-5(1H)-*one*.[1]—The *N*-acetate of Uhlé's ketone [1] (15 mg) in xylene (10 ml) was heated under reflux with 10% palladium–charcoal (20 mg) for 18 h. The mixture was filtered hot and the filtrate concentrated *in vacuo* to *ca.* 1 ml. G.l.c. (t_R 16.5 min) and t.l.c. [in $CHCl_3$–EtOH (50 : 1) and EtOAc–light petroleum (1 : 1)] analysis revealed the presence of 1-acetylbenz[*cd*]indol-5(1*H*)-one, an authentic sample of which was prepared by acetylation of benz[*cd*]indol-5(1*H*)-one [1] (t_R 7.5 min).

We thank the S.R.C. for a studentship (to G. M. B.) and the Physico-Chemical Measurements Unit, Aldermaston, for ^{13}C n.m.r. data.

[5/972 *Received*, 22*nd May*, 1975]