1,3,4,5-Tetrahydrobenz[*c,d*]indoles and Related Compounds. Part IV.[1] Attempted Syntheses of Lysergic Acid

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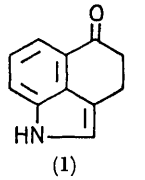
Attempts to devise a synthesis of lysergic acid from 3,4-dihydrobenz[*c,d*]indol-5(1*H*)-one (I) *via* methyl *N*-acetonyl-*N*-{1,3,4,5-tetrahydro-5-oxo-1-(*p*-tolylsulphonyl)benz[*c,d*]indol-4-yl}carbamate (23) failed owing to difficulties in cyclising the latter to the tetracyclic ketone (4).

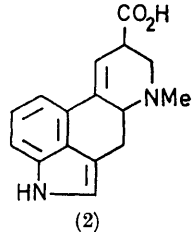
Several alternative routes were examined and, *inter alia*, 4,8,9,10a-tetrahydro-9-(hydroxymethyl)-9-methyl-6*H*-indolo[3,4-*gh*][1,4]benzoxazinium chloride (30) and 4-acetyl-6,6a,7,8-tetrahydro-8-imino-4*H*-indolo[6,5,4-*cd*]-indolium acetate (40) have been prepared.

In Part I [2] of this series we described an improved synthesis of Uhle's ketone [3] (1) required as a starting point for the preparation of potential therapeutic agents and for a projected synthesis of lysergic acid (2).

In this paper we report our efforts, as yet unsuccessful, to synthesise the tetracyclic ketones (3) and (4) where R^1 is a suitable protecting group, which (following the example of R. B. Woodward and the Lilly Group [4] in the corresponding indoline series) might be converted into lysergic acid. Although we have investigated possible routes to both ketones (3) and (4) we were particularly interested in the latter because of our expectation that these neutral ketones would be more stable than their basic counterparts and therefore more amenable to further chemical manipulations. The first section of this paper is concerned with the synthesis of the precursor diketones (5) and the latter section with some other approaches.



(1)



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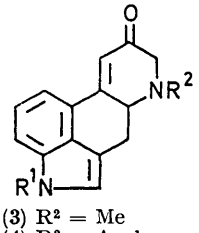
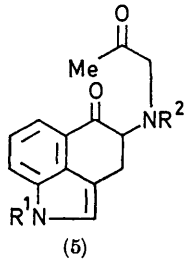
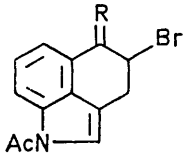


(3) R^2 = Me
(4) R^2 = Acyl

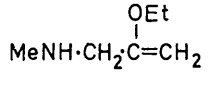


(5)

The most direct route to compound (5; R^2 = Me) (following Woodward and his co-workers [4]) would be treatment of the bromo-ketone (6) [5] with methylaminoacetone ethylene acetal or the less sterically hindered β-ethoxyallylmethylamine (8) followed by acid hydrolysis. However our difficulties [6] in carrying out such reactions with even simple bases discouraged us, although Uhle had reported [5] that he had achieved such a condensation using β-methylaminopropionitrile. In the event, we were unable to isolate in a pure condition any basic materials from the reaction of the bromo-ketone (6) or its acetal (7) with any of these bases; an additional complication in these reactions is the lability of the 1-acetyl grouping.



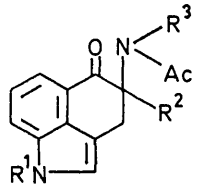
(6) R = O
(7) R = $[CH_2]_2O_2$



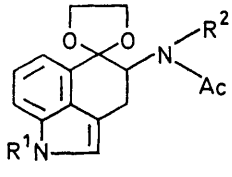
(8)

We next examined the possibility of introducing the required *N*-acetonyl function as in (5) *via* an amide-alkylation reaction, and in the first instance studied more simple examples involving *N*-methylation.

The 1-acetyl-4-acetamido-ketone (8), readily prepared from the 4-bromo-ketone (6) [5] by conversion into the 4-azido-compound and subsequent reduction and acetylation, formed a sodio-derivative which reacted smoothly with methyl iodide, but the product was a complex mixture which we were unable to separate. The corresponding acetal (9), on the other hand, on treatment with sodium hydride (1 mol. equiv.) and methyl iodide furnished crystalline material identified from its i.r. spectrum and analysis as the 1-methyl acetal (10). We have



(8) R^1 = Ac, R^2 = R^3 = H
(11) R^1 = R^2 = R^3 = H
(12) R^1 = R^2 = Me, R^3 = H
(16) R^1 = CH_2Ph, R^2 = H, R^3 = Me



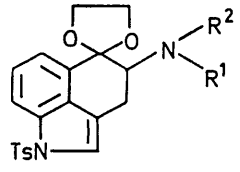
(9) R^1 = Ac, R^2 = H
(10) R^1 = Me, R^2 = H
(13) R^1 = R^2 = H
(14) R^1 = CH_2Ph, R^2 = H
(15) R^1 = CH_2Ph, R^2 = Me

[1] Part III, R. E. Bowman, D. D. Evans, J. Guyett, H. Nagy, J. Weale, and D. J. Wyeell, *J.C.S. Perkin I*, 1973, 483.
[2] Part I, R. E. Bowman, T. G. Goodburn, and A. A. Reynolds, *J.C.S. Perkin I*, 1972, 1121.
[3] F. C. Uhle, *J. Amer. Chem. Soc.*, 1949, **71**, 761.
[4] E. C. Kornfield, E. J. Fornefeld, G. B. Kline, M. J. Mann, D. E. Morrison, R. G. Jones, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1956, **78**, 3087.
[5] F. C. Uhle, *J. Amer. Chem. Soc.*, 1951, **73**, 2402.
[6] Part II, R. E. Bowman, D. D. Evans, J. Guyett, H. Nagy, J. Weale, and A. C. White, *J.C.S. Perkin I*, 1972, 1926.

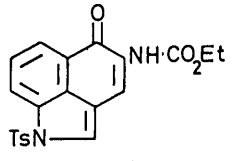
already reported [6] a similar replacement of an indole 1-acetyl group by methyl under the same conditions, but at that time this curious reaction was new to us. Methylation of the unprotected 4-acetamido-indolic ketone (11) with sodium hydride (2 mol. equiv.) and excess of methyl iodide gave a high yield of the 1,4-dimethyl derivative (12) in which both N-1 and C-4 alkylation had occurred. It was now clear that in order to obtain N-4 alkylation, a less labile group at the 1-position and deactivation of the carbonyl grouping was required. To this end, the acetamido-acetal (13) was prepared and converted into its 1-benzyl derivative (14), which was then treated with sodium hydride–methyl iodide as before. The product, formed in high yield, was the required 1-benzyl-4-*N*-methylacetamido-acetal (15), which was readily converted by treatment with toluene-*p*-sulphonic acid in acetone into the parent ketone (16).

Nevertheless the use oft he 1-benzyl group was not considered satisfactory for further work on account of problems likely to arise during its removal, and it was at this stage that we investigated and subsequently introduced the use of the tosyl group for N-1 blocking in indoles; [1,6,7] a particular advantage of this protecting group is that it is resistant to many reagents including anhydrous bases and yet readily removable with hot aqueous alkali.

Treatment of 4-azido-3,4-dihydro-1-tosylbenz[*c*,*d*]indol-5(1*H*)-one [1] with ethylene glycol in the presence of boron trifluoride–ether complex furnished in high yield the corresponding 5-acetal, which was not obtained crystalline. Reduction either with lithium aluminium hydride or catalytically with hydrogen and palladised charcoal, gave in reasonable yield the crystalline amino-acetal (17), a key intermediate in much of our subsequent work. With methyl chloroformate, it gave a crystalline



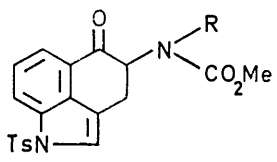
(17) $R^1 = R^2 = H$
(18) $R^1 = H$, $R^2 = CO_2Me$
(19) $R^1 = H$, $R^2 = CO_2Et$
(20) $R^1 = CH_2{\cdot}C{\equiv}CH$, $R^2 = CO_2Me$



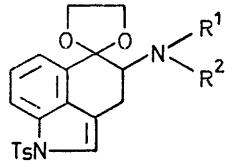
(21)

urethane methyl ester (18) and with ethyl chloroformate an oily urethane (19) which was converted by treatment with 20N-sulphuric–acetic acids in the presence of air into the relatively high melting, intensely yellow 3,4-didehydro-urethane (21). These amido-acetals could also be prepared in high yield by acetalisation of the parent amido-ketone, but unlike those obtained from the colourless amino-acetal (17), they were yellow, owing, we suspect, to some aerial oxidation to the 3,4-didehydro-derivative despite routine use of an inert atmosphere during their preparation; the ready aerial oxidation of 4-anilino-3,4-dihydro-1-tosylbenz[*c*,*d*]indol-5(1*H*)-one to the corresponding 3,4-didehydro-compound has already been reported by us.[6]

We chose the crystalline methyl urethane (18) for our amide-alkylation reactions because model experiments (as yet unpublished) had shown that sodio-derivatives of urethanes gave higher and more reliable yields in such alkylations than did the corresponding sodio-acetamido-compounds, particularly when reagents such as prop-2-ynyl bromide were used. In the event, the sodio-derivative of the acetal urethane (18) reacted smoothly with prop-2-ynyl bromide to give the *N*-prop-2-ynyl compound (20), which could be converted by controlled treatment with dilute sulphuric acid in hot dioxan into the corresponding acetylenic ketone (22); a similar reaction carried out in the presence of mercury(II) sulphate gave the required diketone [(23) ≡ (5; R^1 = Ts, $R^2 = CO_2Me$)].



(22) $R = CH_2{\cdot}C{\equiv}CH$
(23) $R = CH_2{\cdot}COMe$



(24) $R^1 = R^2 = CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$
(25) $R^1 = H$, $R^2 = CH_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}OH$
(26) $R^1 = Me$, $R^2 = CH_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}OH$
(27) $R^1 = Me$, $R^2 = CH_2{\cdot}COMe$
(28) $R^1 = R^2 = CH_2{\cdot}C(OEt){=}CH{\cdot}CO_2Et$

Up to the time when this work had to be terminated, we were unable to ring close this diketone (23) to the tetracyclic ketone system (4). However our more recent success in effecting similar closures in model systems with methyl magnesium carbonate,[8] suggests that this conversion (23) ⟶ (4) might be possible, but it remains untried.

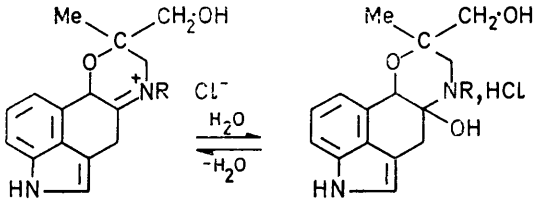
At the same time we investigated the possible synthesis of the basic diketone (5; R^1 = Ts, R^2 = Me) with a view to ring closure to the tetracyclic ketone (3). Reaction of the 1-tosyl-4-amino-acetal (17) with 2,3-epoxypropan-1-ol furnished the tetraol (24), but with 2,3-epoxy-2-methylpropan-1-ol it gave the crystalline diol (25) in high yield. *N*-Methylation of the latter with methyl iodide in the presence of potassium hydrogen carbonate took place readily to give the *N*-methylamino-diol (26) which could not be crystallised; it did however react smoothly with periodic acid to give the *N*-acetonylmethylamino-acetal (27), isolated as its hydrochloride monohydrate. Attempts to remove the acetal group in acidic medium proved unrewarding, the amino-acetal (27) being relatively stable under mild conditions and resinified by strong acids, a result not unexpected on account of similar difficulties encountered [4] in the corresponding indoline series.

In anticipation of the greater lability of the acetal

[7] R. E. Bowman, D. D. Evans, and P. J. Islip, *Chem. and Ind.*, 1971, 33.

[8] R. E. Bowman, R. I. Thrift, J. Weale, and A. C. White, *J.C.S. Perkin I*, 1972, 2878.

group once the 1-' acyl ' substituent had been removed,[6] the *N*-methyl diol (26) was treated with hot alkali to remove the tosyl group and the product was dissolved in dilute hydrochloric acid to hydrolyse the acetal. The resulting solution slowly deposited a crystalline salt whose analytical figures were those calculated for the expected indole-ketol less one mole of water; the unmethylated amino-diol (25) gave a similar compound.



(29) R = Me
(30) R = H

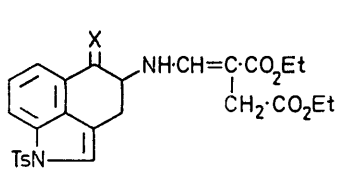
(31) R = Me
(32) R = H

On the basis of i.r. (absence of CO bands) and u.v. (no ' styrene '-like absorption) spectra and the analytical data, these compounds are formulated as the benzoxazinium salts (29) and (30), respectively. However both salts form acidic solutions in aqueous ethanol and such solutions may be titrated with sodium hydroxide to yield equivalent weight values. It seems likely therefore that in such media, these salts exist largely or wholly in the carbinolamine forms (31) and (32) and that the determined pK_a values of 5·79 and 6·40 refer to these forms.

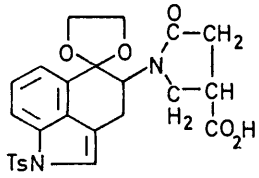
In an attempt to prepare a β-keto-ester related to the *N*-acetonyl acetal (27), the amino-acetal (17) was treated with ethyl γ-bromo-β-ethoxycrotonate, but the only isolable crystalline product was the diester (28).

An alternative approach to lysergic acid, originally attempted by Stoll and his co-workers,[9] would be to prepare an appropriately substituted 5-ketone carrying an aminomethylsuccinate substituent at the 4-position, and to attempt a Stobbe condensation to form ring D. Condensation of 4-amino-3,4-dihydro-1-tosylbenz[*c*,*d*]-indol-5(1*H*)-one with diethyl formylsuccinate furnished a yellow crystalline condensation product which from its i.r. and u.v. spectra must have the ' aminomethylene ' (33) rather than the isomeric Schiff's base structure. Catalytic reduction of this ester in ethanolic solution over palladised charcoal took place with absorption of 1 mol. equiv. of hydrogen to give the 5-hydroxy-ester (34); over platinum further absorption of hydrogen occurred and although no pure product was isolated, there was convincing evidence from u.v. spectra that reduction of the indole nucleus was taking place rather than that of the aminomethylene grouping. The amino-acetal (17) reacted with itaconic acid monomethyl ester to give the pyrrolidone (25) but this route was not pursued.

Finally, we examined methods for the formation of C–C bonds at the 5-position. The known 5-hydroxyurethane (26) [1] was easily converted into the corresponding 5-bromo-compound (37) with anhydrous hydrogen bromide, but despite many attempts under various conditions, this could not be converted into the 5-cyano-derivative (38); it seems likely that steric hindrance is responsible for this difficulty since other reagents such as

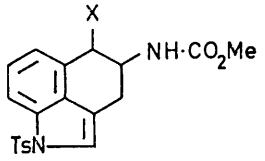


(33) X = O
(34) X = H,OH



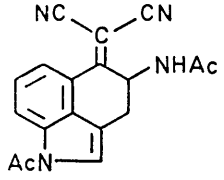
(35)

hydrogen–Raney nickel or –palladised charcoal did not displace the 5-bromo-atom, though sodium azide did.



(36) X = OH
(37) X = Br
(38) X = CN

In an effort to introduce a C_2 chain at C-5 in the presence of an amide substituent at C-4, Reformatsky reagents and ethoxyethynylmagnesium bromide were tried without success, but Cope reactions proceeded remarkably well. Thus, 4-acetamido-1-acetyl-3,4-dihydrobenz[*c*,*d*]indol-5(1*H*)-one (8) reacted easily with malononitrile to give the unsaturated dinitrile (39); with ethyl cyanoacetate further reactions involving hydrolysis, deacetylation, decarboxylation and ring closure occurred and the product which separated from the reaction mixture at 140° was the tetracyclic acetate salt (40). In the *N*-tosyl ketone series, the normal products (41)—(43)



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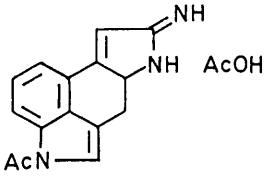

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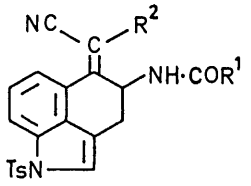

(41) R^1 = Me, R^2 = CN
(42) R^1 = OMe, R^2 = CN
(43) R^1 = OMe, R^2 = CO_2Et

were obtained. Many of these compounds had m.p.s higher than 330° and were of little further use to us as all attempts to bring about reduction of the αβ-unsaturated linkage either catalytically or with alkali metal borohydrides failed, owing presumably to a high degree of steric hindrance near this linkage.

EXPERIMENTAL

Unless stated otherwise, i.r. spectra of solids were determined for Nujol mulls and those of oils for liquid films; u.v. spectra were measured for solutions in ethanol. Potentiometric titrations were carried out in aqueous ethanol (1 : 1).

[9] A. Stoll, J. Rutschmann, and Th. Petrzilka, *Helv. Chim. Acta*, 1950, **33**, 2257.

α-*Ethoxy*-N-*methylacrylamide*.—Ethyl α-ethoxyacrylate (30 g) was added to aqueous methylamine (40%; 100 ml) and the mixture left at room temperature for 24 h. Evaporation to dryness at 15 mmHg and distillation of the residue furnished the *amide* (25 g), b.p. 90—91° at 0·7 mmHg as an oil which rapidly solidified. Crystallisation from light petroleum containing a little benzene gave needles, m.p. 49—49·5°, $\nu_{max.}$ 3350, 1680, and 1620 cm^{-1} (Found: C, 56·2; H, 8·4; N, 11·0. $C_6H_{11}NO_2$ requires C, 55·8; H, 8·6; N, 10·9%).

2-*Ethoxyallylmethylamine*.—A solution of the preceding amide (24 g) in warm ether (70 ml) was added with stirring under nitrogen to lithium aluminium hydride (10 g) in ether during 25 min. The mixture was boiled under reflux for 7 h and decomposed with ice cooling, by addition of 5N-sodium hydroxide (10 ml) and then water (10 ml). Work-up in the usual manner followed by distillation through a Fenske column fitted with a reflux head, yielded the *amine* (11·5 g), b.p. 126—132°, $\nu_{max.}$ 3350 and 1650 cm^{-1} (Found: C, 62·3; H, 11·3; N, 12·2. $C_6H_{13}NO$ requires C, 62·5; H, 11·4; N, 12·2%).

1-*Acetyl*-4-*bromo*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydrobenz*[c,d]*indole* (7).—A solution of the parent bromo-ketone [5] (6) (4·65 g) in benzene (75 ml) containing a toluene-*p*-sulphonic acid (100 mg) and ethylene glycol (4 ml) was refluxed in a flask fitted with a water separator until no further water was collected (4 h). The cooled mixture was treated with charcoal and anhydrous potassium carbonate and filtered. Evaporation yielded the *acetal* (3·9 g) as needles (from benzene–light petroleum; twice), m.p. 146—147°, $\nu_{max.}$ 1694 cm^{-1} (Found: C, 53·9; H, 4·1; Br, 24·3; N, 4·2. $C_{15}H_{14}BrNO_3$ requires C, 53·6; H, 4·2; Br, 23·9; N, 4·2%).

1-*Acetyl*-4-*azido*-3,4-*dihydrobenz*[c,d]*indol*-5(1H)-*one*.—Sodium azide (3·9 g) in water (20 ml) was added with stirring and cooling to a solution of the corresponding bromo-ketone [5] (6) (8·8 g) in dimethylformamide (65 ml) containing acetic acid (4 ml) previously cooled to 0°. A rapid evolution of heat occurred and crystals appeared. Filtration and washing with water yielded the yellow-orange *azido-ketone* (6·5 g), m.p. 146—147° (decomp.). This material was sufficiently pure for subsequent experiments but crystallised from aqueous dimethylformamide or a large volume of ethanol, m.p. 150—151°, $\nu_{max.}$ 2150 (N_3), 1700 (indole NAc), and 1600 cm^{-1} (Found: C, 61·1; H, 3·8; N, 22·4. $C_{13}H_{10}N_4O_2$ requires C, 61·4; H, 4·0; N, 22·0%).

1-*Acetyl*-4-*amino*-3,4-*dihydrobenz*[c,d]*indol*-5(1H)-*one Hydrochloride*.—A suspension of the preceding azido-ketone (4·5 g) and 10% palladium–charcoal (1 g) in ethanol (100 ml) containing concentrated hydrochloric acid (5 ml) was shaken in hydrogen at room temperature and pressure. Filtration yielded a mixture of product and catalyst (4·9 g) which on extraction with boiling water and addition of concentrated hydrochloric acid to the cooled extract furnished the *hydrochloride* (3·1 g) as pale yellow needles, m.p. 246—247° (decomp.), $\nu_{max.}$ 1690 cm^{-1}, pK_a 6·98 (Found: C, 59·3; H, 5·0; N, 10·8; Cl, 13·4%; equiv., 264. $C_{13}H_{13}ClN_2O_2$ requires C, 59·1; H, 4·9; N, 10·6; Cl, 13·4%; equiv., 265).

The N-*acetyl* derivative (8) formed pale yellow needles (from ethanol), m.p. 244—246° (decomp.), $\lambda_{max.}$ 225 (ε 17,380), 256 (19,300), 302 (11,650), and 328 (4690) nm, $\nu_{max.}$ 3300 (NH), 1710 (indole NAc), 1676 (CO), 1635 (amide I), and 1530 (amide II) cm^{-1} (Found: C, 66·8; H, 5·4; N, 10·0. $C_{15}H_{14}N_2O_3$ requires C, 66·7; H, 5·2; N, 10·4%).

This compound could be obtained more conveniently by conducting the hydrogenation in acetic acid containing acetic anhydride.

4-*Acetamido*-3,4-*dihydrobenz*[c,d]*indol*-5(1H)-*one* (11).—A suspension of the diacetyl compound (8) (160 mg) in 2N-sodium hydroxide (10 ml) and ethanol (5 ml) was heated at 75° for 10 min and the clear red solution was brought to pH 5 with acetic acid. Isolated with ethyl acetate, the *amide* was obtained as yellow needles (from benzene), m.p. 196—198° (lit.,[9] 205—207°), $\nu_{max.}$ 3350 and 3300sh (NH), 1682 (CO), 1645 (amide I), and 1520 (amide II) cm^{-1} (Found: C, 68·1; H, 5·2; N, 12·2. Calc. for $C_{13}H_{12}N_2O_2$: C, 68·4; H, 5·3; N, 12·3%).

4-*Acetamido*-3,4-*dihydro*-1,4-*dimethylbenz*[c,d]*indol*-5(1H)-*one* (12) (with D. J. Weyell).—The foregoing amide (5·57 g) was added to a suspension of sodium hydride (1·6 g) in benzene–dimethylformamide (1 : 5; 100 ml) whereupon gas was evolved and during 15 min a clear solution was obtained. Methyl iodide (10 ml) was then added slowly with cooling. The mixture was heated at 50° for 1 h and then evaporated to dryness *in vacuo*. Addition of water yielded the *acetamido-ketone* (4·85 g), m.p. 223—226°, which crystallised from acetonitrile with m.p. 225—226°, $\nu_{max.}$ 3340 (NH), 1680 (CO), 1640 (amide I), and 1515 (amide II) cm^{-1} (Found: C, 70·4; H, 6·2; N, 10·8. $C_{15}H_{16}N_2O_2$ requires C, 70·3; H, 6·3; N, 10·9%).

4-*Acetamido*-1-*acetyl*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydrobenz*[c,d]*indole* (9).—The parent ketone (8) (3·7 g) was acetalised as previously with chloroform as solvent during 24 h to give the *acetal* (2·6 g) as rhombs (from ethanol), m.p. 244—245°, $\nu_{max.}$ 3380 (NH), 1680 (indole NAc), 1660 (amide I), and 1535 (amide II) cm^{-1} (Found: C, 64·8; H, 5·7; N, 8·9. $C_{17}H_{18}N_2O_4$ requires C, 65·0; H, 5·8; N, 8·9%).

4-*Acetamido*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-*methylbenz*[c,d]*indole* (10).—The preceding acetal was treated successively with sodium hydride (1·0 mol. equiv.) and excess of methyl iodide as described for (12) to give the 1-*methyl acetal* as rhombs (from carbon tetrachloride), m.p. 166—167°, $\lambda_{max.}$ 204 (ε 24,500), 227 (33,200), and 294 (7030) nm, $\nu_{max.}$ 3300 (NH), 1640 (amide I), and 1535 (amide II) cm^{-1} (Found: C, 67·0; H, 6·3; N, 9·9. $C_{16}H_{18}N_2O_3$ requires C, 67·1; H, 6·3; N, 9·8%).

4-*Acetamido*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydrobenz*[c,d]*indole* (13).—The corresponding diacetyl compound (9) was treated with 2N-sodium hydroxide as in the preparation of compound (11) to give the *amide* as rhombs (from ethyl acetate), m.p. 196—197°, $\lambda_{max.}$ 203 (ε 21,300), 224 (34,600), 286 (6980), and 292 (6930) nm, $\nu_{max.}$ 3410, 3250, 1642 (amide I), and 1530 (amide II) cm^{-1} (Found: C, 66·1; H, 6·1; N, 10·4. $C_{15}H_{16}N_2O_3$ requires C, 66·2; H, 5·9; N, 10·3%).

4-*Acetamido*-1-*benzyl*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydrobenz*[c,d]*indole* (14).—The preceding amide was converted into its sodio-derivative and treated with benzyl chloride as previously. The N-*benzyl acetal* formed needles (from benzene–light petroleum), m.p. 235—236°, $\lambda_{max.}$ 206 (ε 22,400), 227 (23,400), and 293 (ε 5400) nm, $\nu_{max.}$ 3300 (NH), 1640 (amide I), and 1530 (amide II) cm^{-1} (Found: C, 73·1; H, 6·0; N, 7·8. $C_{22}H_{22}N_2O_3$ requires C, 72·9; H, 6·1; N, 7·7%).

1-*Benzyl*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-4-(N-*methylacetamido*)*benz*[c,d]*indole* (15).—The parent amide (14) on methylation with methyl iodide–sodium hydride as before, gave the N-*methylamide*, cream rhombs (from benzene–light petroleum), m.p. 186—188°, $\lambda_{max.}$ 206 (ε 35,500), 227 (33,500), and 294 (7640) nm, $\nu_{max.}$ 1630 (CO·N<) cm^{-1}

(Found: C, 73·5; H, 6·5; N, 7·8. $C_{23}H_{24}N_2O_3$ requires C, 73·4; H, 6·4; N, 7·4%).

1-*Benzyl*-3,4-*dihydro*-4-(N-*methylacetamido*)*benz*[c,d]*indol*-5(1H)-*one* (16).—A solution of the foregoing acetal (250 mg) in acetone (10 ml) containing toluene-*p*-sulphonic acid (25 mg) was boiled under reflux for 7 h. Removal of solvent *in vacuo* gave a brown oil which crystallised from aqueous propan-2-ol as microneedles, m.p. 146—147·5°, $\lambda_{max.}$ 206 (ε 35,700), 254 (1700), 330 (4600), and 365 (5090) nm, $\nu_{max.}$ 1680 (CO) and 1633 (CO·N<) cm^{-1} (Found: C, 75·5; H, 6·2; N, 8·3. $C_{21}H_{20}N_2O_2$ requires C, 75·9; H, 6·1; N, 8·4%).

4-*Amino*-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indole* (17).—Freshly distilled boron trifluoride–ether (58 ml) was added to a suspension of 4-azido-3,4-dihydro-1-(*p*-tolylsulphonyl)benz[*c,d*]indol-5(1*H*)-one [1] (16·8 g) in chloroform (600 ml) containing ethylene glycol (58 ml); the mixture was stirred under nitrogen for 28 h then poured slowly into an excess of aqueous sodium hydrogen carbonate with stirring. The chloroform extract was washed with water, dried, and evaporated to dryness *in vacuo* to give a red viscous oil, $\nu_{max.}$ 2150 (N_3) cm^{-1}. Traces of remaining chloroform were eliminated by addition of either toluene or acetic acid [for (b)] and removal *in vacuo*.

(a) *Use of lithium aluminium hydride.* A solution of the crude azido-acetal (2·0 g) in tetrahydrofuran (75 ml) was added to a stirred suspension of lithium aluminium hydride (2 g) in tetrahydrofuran (75 ml) with cooling at 5—10° and stirring was continued for 1 h at the same temperature. The mixture was decomposed with water and 4N-sodium hydroxide and then extracted with ethyl acetate. The organic extract was shaken twice with aqueous citric acid (10%); basification of the aqueous acid extract with 2N-sodium hydroxide furnished an oil which was isolated with ethyl acetate. Crystallisation from ethanol furnished the *amino-acetal* (700 mg), m.p. 150—152°, $\nu_{max.}$ 1595 cm^{-1} pK_a 7·52 (Found: C, 62·5; H, 5·4; N, 7·2. $C_{20}H_{20}N_2O_4S$ requires C, 62·5; H, 5·2; N, 7·3%).

The following derivatives were prepared: N-*acetyl*, prisms (from ethanol), m.p. 226° (decomp.), $\nu_{max.}$ 3300 (NH) and 1645 (amide) cm^{-1} (Found: C, 61·6; H, 5·0; N, 6·7. $C_{22}H_{22}N_2O_5S$ requires C, 62·0; H, 5·2; N, 6·6%); N-*methoxycarbonyl* (18), needles (from methanol), m.p. 141—143°, $\nu_{max.}$ 3350 (NH), 1700 (amide I), and 1540 (amide II) cm^{-1} (Found: C, 59·9; H, 5·1; N, 6·4. $C_{22}H_{22}N_2O_6S$ requires C, 59·7; H, 5·0; N, 6·3%); N-*benzyloxycarbonyl*, prisms (from methanol), m.p. 132—134° (Found: C, 64·6; H, 5·2; N, 5·1. $C_{28}H_{26}N_2O_6S$ requires C, 64·9; H, 5·1; N, 5·4%).

The *N*-acetyl and *N*-methoxycarbonyl derivatives were also prepared from the parent ketones by acetalisation ($CHCl_3$; 30 h).

(b) *Catalytic reduction.* 10% Palladium–charcoal (8 g) was added to a solution of the crude acetal (18 g) in acetic acid (500 ml) and the mixture stirred in a 2 l flask under hydrogen at normal temperature and pressure for 3 h (flask evacuated and refilled with fresh hydrogen twice during this time). Filtration, evaporation, and work-up as in (a) yielded the product (9·8 g), m.p. 151—152°.

Acidic Hydrolysis of the Acetal Carbamate (19) *in the Presence of Air.*—The preceding amino-acetal was converted into its *N*-ethoxycarbonyl derivative (19), an oil which resisted crystallisation ($\nu_{max.}$ 3355 and 1700 cm^{-1}). The oily urethane (860 mg) was dissolved in acetic acid (10 ml) containing 20N-sulphuric acid (4 ml) and the mixture was left in a stoppered flask (250 ml) for 24 h. Filtration gave yellow crystals (60 mg); the filtrate, after a further 24 h under the same conditions, gave a further crop (60 mg). This process was repeated three times in all to give *ethyl* 1,5-*dihydro*-5-*oxo*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indol*-4-*ylcarbamate* (21) (180 mg), yellow needles (from acetonitrile), m.p. 193—195°, $\nu_{max.}$ 3350 (NH), 1703 (amide I), 1630 (conj. CO), 1600, and 1505 (amide II) cm^{-1} (Found: C, 61·6; H, 4·5; N, 6·9. $C_{21}H_{18}N_2O_5S$ requires C, 61·5; H, 4·4; N, 6·8%).

For comparison, a sample of the 3,4-*dihydro-analogue* was prepared.[1] It crystallised from ethanol as pale yellow prisms, m.p. 144—146°, $\nu_{max.}$ 3400 (NH), 1702 (amide I), 1690 (CO), and 1520 (amide II) cm^{-1} (Found: C, 61·6; H, 4·7; N, 6·7. $C_{21}H_{20}N_2O_5S$ requires C, 61·2; H, 4·9; N, 6·8%).

Methyl N-{5,5-*Ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indol*-4-*yl*}-N-*prop*-2-*ynylcarbamate* (20).—Sodium hydride (50% oil dispersion; 792 mg) was added to a solution of the urethane (18) (6·6 g) in benzene–dimethylformamide (1 : 2; 150 ml) with stirring under nitrogen. After 1 h a clear solution was obtained, whereupon freshly distilled prop-2-ynyl bromide (4 ml) was added. The mixture was neutral 30 min later and solvents were then removed at 50° and 1 mmHg. The product was isolated with benzene and obtained as a glassy froth which after extraction with light petroleum to remove mineral oil, crystallised slowly from methanol (50 ml) as prisms, m.p. 153—157°. Further crystallisation from methanol gave the *urethane*, m.p. 158—159°, $\nu_{max.}$ 3350 and 2120 (C≡C), and 1700 (amide I) cm^{-1} (Found: C, 62·6; H, 5·1; N, 5·9. $C_{25}H_{24}N_2O_6S$ requires C, 62·5; H, 5·0; N, 5·8%).

Methyl N-*Acetonyl*-N-{1,3,4,5-*tetrahydro*-5-*oxo*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indol*-4-*yl*}*carbamate* (23).—A solution of the acetal (20) (5·2 g) in purified dioxan (200 ml) and 2N-sulphuric acid (50 ml) was heated in the presence of mercury(II) sulphate (450 mg) at 90° for 45 min. After dilution with water, dioxan was removed *in vacuo* and the *product* was isolated with chloroform, as a foam which crystallised from hot methanol (25 ml) as pale yellow prismatic needles (2·7 g), m.p. 159—161°, $\nu_{max.}$ 1725 (MeCO), 1700 (amide I), and 1690 (CO) cm^{-1} (Found: C, 61·0; H, 5·1; N, 6·2. $C_{23}H_{22}N_2O_6S$ requires C, 60·8; H, 4·9; N, 6·2%).

Methyl N-{1,3,4,5-*Tetrahydro*-5-*oxo*-1-(p-*tolylsulphonyl*)-*benz*[c,d]*indol*-4-*yl*}-N-*prop*-2-*ynylcarbamate* (22).—A solution of the acetal (20) (500 mg) in purified dioxan (20 ml) containing 2N-sulphuric acid (5 ml) was heated at 90° under nitrogen for 45 min and poured into water (100 ml). The *product* (450 mg) obtained by filtration and trituration with ether, crystallised from methanol (3 ml) as prisms of an ether complex, m.p. *ca.* 92° (frothing), $\nu_{max.}$ 3300 and 2120 (C≡C), 1702 (amide I), and 1690 (CO) cm^{-1} (Found: C, 63·2; H, 5·5; N, 5·9. $C_{23}H_{20}N_2O_5S$,Et_2O requires C, 63·5; H, 5·9; N, 5·5%).

4-[*Bis*-(2,3-*dihydroxypropyl*)*amino*]-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indole* (24).—A solution of the amino-acetal (17) (370 mg) and 2,3-epoxypropan-1-ol (225 mg) in ethyl acetate (2 ml) was boiled under reflux for 6 h and solvent was removed *in vacuo* to give the *product* (120 mg) as plates (from hot dioxan) of a dioxan complex, m.p. 132—133°, $\nu_{max.}$ 3550 and 3400 cm^{-1}, pK_a 5·25 (Found: C, 57·7; H, 6·4; N, 4·4. $C_{26}H_{32}N_2O_8S$,$C_4H_8O_2$ requires C, 58·1; H, 6·5; N, 4·5%). It was converted by treatment with pyridine–acetic anhydride into its *tetra-acetyl ester*, prisms (from methanol), m.p. 174—175°, $\nu_{max.}$ 1722 and 1715 cm^{-1}

(Found: C, 58·2; H, 5·8; N, 4·1. $C_{34}H_{40}N_2O_{12}S$ requires C, 58·2; H, 5·7; N, 4·0%).

4-(2,3-*Dihydroxy*-2-*methylpropylamino*)-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indole* (25).—A solution of the amino-acetal (17) (3·5 g) and 2,3-epoxy-2-methylpropan-1-ol (1·1 ml) in xylene (17 ml) was boiled under reflux for 20 h and allowed to cool; the *product* (3·5 g) crystallised, m.p. 137—138°, $\lambda_{max.}$ 220 (ε 24,400), 260 (12,000), and 294 (2000) nm, $\nu_{max.}$ 3450—3350 and 3015 cm^{-1}, pK_a 6·35 (Found: C, 61·2; H, 6·1; N, 5·7%; equiv., 470. $C_{24}H_{28}N_2O_6S$ requires C, 61·0; H, 6·0; N, 5·9%; equiv., 472).

4-[N-(2,3-*Dihydroxy*-2-*methylpropyl*)*methylamino*]-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]-*indole* (26).—Potassium hydrogen carbonate (1 g) and methyl iodide (4 ml) were added to a solution of the preceding diol (472 mg) in ethyl acetate (8 ml); the mixture was boiled with stirring under reflux for 6 h, cooled, filtered from inorganic material (1 equiv. I^- by titration), and evaporated to dryness. All attempts to induce the resulting glass (473 mg) to crystallise failed.

4-(N-*Acetonylmethylamino*)-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indole Hydrochloride* (27).—The preceding crude oil (3·2 g) was dissolved in 0·2N-sulphuric acid (100 ml) and 0·5N-sodium periodate (18 ml) was added during 5 min. The mixture was stirred at room temperature for 1 h and sodium hydrogen carbonate (2·5 g) was added. Isolation with ethyl acetate gave the free amine (2·75 g) as a foam which was dissolved in ethyl acetate (15 ml) and ethereal hydrogen chloride was added. The crude salt (2·8 g) which separated was purified by dissolution in chloroform and careful addition of ether; a hydrated salt of variable composition was deposited. On drying at 60° and 1 mmHg for 5 h, the *keto-acetal monohydrate*, was obtained; m.p. 128—129°, $\lambda_{max.}$ 218 (ε 30,500), 260 (15,600), and 284 (6900) nm, $\nu_{max.}$ 3400br and 1720 (CO) cm^{-1}, pK_a 4·85 (Found: C, 56·6; H, 5·9; N, 5·5. $C_{24}H_{27}ClN_2O_5S,H_2O$ requires C, 56·6; H, 5·7; N, 5·5%).

4,8,9,10a-*Tetrahydro*-9-(*hydroxymethyl*)-9-*methyl*-6H-*indolo*[3,4-gh][1,4]*benzoxazinium Chloride* (30) (with Dr. D. Waite).—The amino-diol (25) (1 g)was added to a solution of potassium hydroxide (300 mg) in ethanol (7 ml); the mixture was boiled under reflux for 3 h, poured in water, and extracted with ethyl acetate. The resulting gum (700 mg) was dissolved in 2N-hydrochloric acid (3 ml) and the solution stored in the dark at 0° for 24 h. The separated *salt* (150 mg) had m.p. 122° (decomp.), $\lambda_{max.}$ 224 (ε 32,800), 287 (7000), and 294 (7100) nm, $\nu_{max.}$ 3250 (NH) cm^{-1}, ' pK_a ' 6·40 (Found: C, 61·2; H, 6·0; N, 9·3%; equiv., 293. $C_{15}H_{17}ClN_2O_2$ requires C, 61·5; H, 5·9; N, 9·6%; equiv., 293).

4,8,9,10a-*Tetrahydro*-9-(*hydroxymethyl*)-7,9-*dimethyl*-6H-*indolo*[3,4-gh][1,4]*benzoxazinium Chloride* (29).—Treatment of the *N*-methylamino-diol (26) in the same manner as in the preceding experiment furnished the *chloride*, needles (from water), m.p. 220° (decomp.) $\lambda_{max.}$ 225 (ε 30,100), 286 (5500), and 295 (5780) nm, $\nu_{max.}$ 3420 and 3180 cm^{-1}, ' pK_a ' 5·79 (Found: C, 62·2; H, 6·4; N, 8·9%; equiv., 305. $C_{16}H_{19}ClN_2O_2$ requires C, 62·4; H, 6·2; N, 9·1%; equiv., 307).

4-[*Bis*-(2-*ethoxy*-3-*ethoxycarbonylprop*-2-*enyl*)*amino*]-5,5-*ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]-*indole* (28).—Potassium hydrogen carbonate (2 g) was added to a mixture of the amino-acetal (17) (1 g), and ethyl γ-bromo-β-ethoxycrotonate (2 g) in ethyl acetate (10 ml); the suspension was heated at 80° for 20 h, cooled, filtered, and evaporated to dryness *in vacuo*. The residue furnished the *diester* (1·2 g) as prismatic needles, m.p. 136—138° (from methanol), $\nu_{max.}$ 1680 cm^{-1}, pK_a < 4 (Found: C, 61·8; H, 6·3; N, 3·7. $C_{36}H_{44}N_2O_{10}S$ requires C, 62·1; H, 6·4; N, 4·0%).

Diethyl 1,3,4,5-*Tetrahydro*-5-*oxo*-1-(p-*tolylsulphonyl*)*benz*-[c,d]*indol*-4-*ylaminomethylenesuccinate* (33).—Diethyl formylsuccinate (0·65 ml) was added with stirring to a solution of 4-amino-3,4-dihydro-1-(*p*-tolylsulphonyl)benz[*c,d*]indol-5(1*H*)-one hydrochloride [1] (1 g) in 50% aqueous acetic acid (20 ml) at 0°, followed by sodium acetate trihydrate (2·4 g). The red gum which separated slowly solidified. The mixture was diluted with water and filtered to give the *ester* (680 mg) as yellow needles (from methanol), m.p. 105—107°, $\lambda_{max.}$ 229 (ε 23,800), 292 (24,300), and 333 (7500) nm, $\nu_{max.}$ 3259 (NH), 1735 (ester CO), 1693 (CO), and 1664 (NH–C=C–CO_2Et) [10] cm^{-1}, pK_a <2·5 (Found: C, 62·4; H, 5·5; N, 5·2. $C_{27}H_{28}N_2O_7S$ requires C, 61·8; H, 5·4; N, 5·3%).

Diethyl 1,3,4,5-*Tetrahydro*-5-*hydroxy*-1-(p-*tolylsulphonyl*)-*benz*[c,d]*indol*-4-*ylaminomethylenesuccinate* (34).—A solution of the foregoing ester (1·2 g) in acetic acid (30 ml) was shaken in the presence of 10% palladium–charcoal (360 mg) in hydrogen for 1·5 h. After filtration and removal of solvent, the *hydroxy-ester monohydrate* was obtained as yellow prisms (from 90% ethanol), m.p. 95—97°, $\lambda_{max.}$ 219 (ε 33,000), 237 (15,700), 267 (16,800), 289 (22,900), and 329 (1190) nm, $\nu_{max.}$ 3505, 3400—3200, 1720, 1700, and 1660 cm^{-1} (Found: C, 59·4; H, 5·9; N, 4·9. $C_{27}H_{30}N_2O_7S,H_2O$ requires C, 59·6; H, 5·9; N, 5·1%).

1-{5,5-*Ethylenedioxy*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[c,d]*indol*-4-*yl*}-5-*oxopyrrolidine*-3-*carboxylic Acid* (35).—A solution of the amino-acetal (17) (384 mg) and itaconic acid methyl ester [11] (190 mg) in dioxan (10 ml) was boiled under reflux for 20 h and evaporated to dryness *in vacuo*. The residue was treated with ethyl acetate and 0·1N-sodium hydroxide (15 ml). The neutral material (270 mg) appeared to be starting material. Acidification of the alkaline extract and isolation with ethyl acetate furnished the *pyrrolidone* (110 mg) as needles (from 96% ethanol), m.p. 208—210° (decomp.), pK_a 4·74 (Found: C, 60·4; H, 4·9; N, 5·6. $C_{25}H_{24}N_2O_7S$ requires C, 60·5; H, 4·9; N, 5·6%).

Methyl 5-*Bromo*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)-*benz*[c,d]*indol*-4-*ylcarbamate* (37).—A stream of dry hydrogen bromide was passed through a solution of *trans*-1,3,4,5-tetrahydro-5-hydroxy-1-(*p*-tolylsulphonyl)benz[*c,d*]indol-4-ylcarbamic acid, methyl ester [1] (36) (2·2 g) in a mixture of purified dioxan (10 ml) and benzene (220 ml) at 0° for 20 min and then at 20° for 2·5 h. More benzene was then added, followed by ice–water. The organic extract was washed with sodium hydrogen carbonate solution and water, and dried. Removal of solvent *in vacuo* furnished an oil which on trituration with ether yielded the *bromo-compound* as a fawn solid, m.p. 153—156° (decomp.) (Found: C, 51·7; H, 4·6; Br, 17·1. $C_{20}H_{19}BrN_2O_4S$ requires C, 51·8; H, 4·1; Br, 17·3%).

A solution of sodium azide (65 mg) in water (1 ml) was added to a solution of the bromo-compound (100 mg) in acetonitrile (5 ml) and the mixture was left overnight. On dilution with water and isolation with ethyl acetate, there was obtained an oil which showed a very strong i.r. absorption peak at 2230 cm^{-1} (N_3) but which could not be crystallised.

[10] E. A. Braude, *Ann. Reports*, 1945, **42**, 119.
[11] B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Org. Chem.*, 1952, **17**, 116.

4-Acetyl-6,6a,7,8-tetrahydro-8-imino-4H-indolo[6,5,4-cd]*indolium Acetate* (40).—A mixture of 4-acetamido-1-acetyl-3,4-dihydrobenz[*c,d*]indol-5(1H)-one [1] (3 g), ethyl cyanoacetate (9 ml), 15% ammonium acetate in acetic acid (6 ml), and toluene (55 ml) was boiled under reflux. After heating for 12 min a clear solution resulted, and 5 min later solid began to separate. The mixture was boiled in all for 1 h, cooled to 60°, and filtered, and the residue was washed with benzene. The residual *acetate* (2·18 g) had m.p. 203—209° (decomp), $\lambda_{max.}$ 208 (ε 20,300), 242 (33,300), 319 (10,500), and 340 (7700) nm, $\nu_{max.}$ 2366 and 1928 (NH_2^+), 1694 (indole NAc), and 1564 (AcO^-) cm^{-1}, pK_a 5·2 and 6·3 (Found: C, 65·7; H, 5·5; N, 13·5%; equiv., 310. $C_{15}H_{13}N_3O,C_2H_4O_2$ requires C, 65·6; H, 5·5; N, 13·5%; equiv., 311).

When 2N-hydrochloric acid (2·5 ml) was added to a solution of the acetate salt (150 mg) in water (5 ml) the *base hydrochloride* (25 mg) separated. It formed fine needles (from aqueous ethanol), m.p. >330°, $\nu_{max.}$ 1697 cm^{-1} (Found: C, 62·6; H, 5·1; N, 14·4. $C_{15}H_{14}ClN_3O$ requires C, 62·6; H, 5·0; N, 14·6%).

4-Acetamido-1-acetyl-1,3,4,5-tetrahydrobenz[c,d]*indol-5-ylidenemalononitrile* (39).—A mixture of the parent acetamido-ketone [1] (270 mg), malonitrile (1·0 g), 15% ammonium acetate in acetic acid (5 ml), and toluene (10 ml) was heated at 130—140° for 15 min, cooled to 60°, and filtered. The residue was washed with toluene and then ether to give the yellow *nitrile* (240 mg), m.p. >330°, $\nu_{max.}$ 3480 and 3400 (NH), 2200 (CN), 1702 (indole NAc), 1695 (amide I), 1605 (conj. C=C), and 1540 (amide II) cm^{-1} (Found: C, 68·0; H, 4·5; N, 18·4; O, 10·5. $C_{18}H_{14}N_4O_2$ requires C, 67·9; H, 4·4; N, 17·6; O, 10·1%).

4-Acetamido-1,3,4,5-tetrahydro-1-(p-tolylsulphonyl)benz[c,d]*indol-5-ylidenemalononitrile* (41).—This *compound* was obtained as in the previous experiment from 4-acetamido-3,4-dihydro-1-(*p*-tolylsulphonyl)benz[*c,d*]indol-5(1*H*)-one, as needles (from acetonitrile), m.p. >330°, $\nu_{max.}$ 3480 and 3380 (NH), 2220 (CN), 1700 (amide I), 1620 (conj. C=C), and 1540 (amide II) cm^{-1} (Found: C, 64·4; H, 4·2; N, 12·8. $C_{23}H_{18}N_4O_3S$ requires C, 64·2; H, 4·2; N, 13·0%).

Methyl 5-Dicyanomethylene-1,3,4,5-tetrahydro-1-(p-tolylsulphonyl)benz[c,d]*indol-4-ylcarbamate* (42).—A mixture of the parent keto-urethane [1] (1·1 g), 15% ammonium acetate in acetic acid (5 ml), malononitrile (2·0 g), and toluene (20 ml) was refluxed in a flask fitted with a water separator for 40 min and cooled. The solid obtained by filtration was washed with toluene and ether to give the *nitrile ester* (950 mg), m.p. >330°, $\lambda_{max.}$ 238 (ε 38,700), 282 (14,700), and 345 (ε 5590) nm, $\nu_{max.}$ 3480 and 3380 (NH), 2220 (CN), 1730 (amide I), 1620 (conj. C=C), and 1545 (amide II) cm^{-1} (Found: C, 61·9; H, 4·0; N, 12·5. $C_{23}H_{18}N_4O_4S$ requires C, 61·9; H, 4·1; N, 12·6%).

The corresponding 1-(p-*tolylsulphonyl*) *cyano-diester* (43), obtained similarly, had m.p. 280—282° (decomp.), $\nu_{max.}$ 3015, 2230 (CN), 1725 (amide I), 1715 (ester CO), 1620 (conj. C=C), and 1540 (amide II) cm^{-1} (Found: C, 61·2; H, 4·6; N, 8·8. $C_{25}H_{23}N_3O_6S$ requires C, 60·9; H, 4·7; N, 8·5%).

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