

Heterodiene Syntheses. Part XVI.¹ A New [4 + 2] Cycloaddition Pathway in the Reaction of 2-Oxoindolin-3-ylideneacetophenones with Ethyl Vinyl Ether

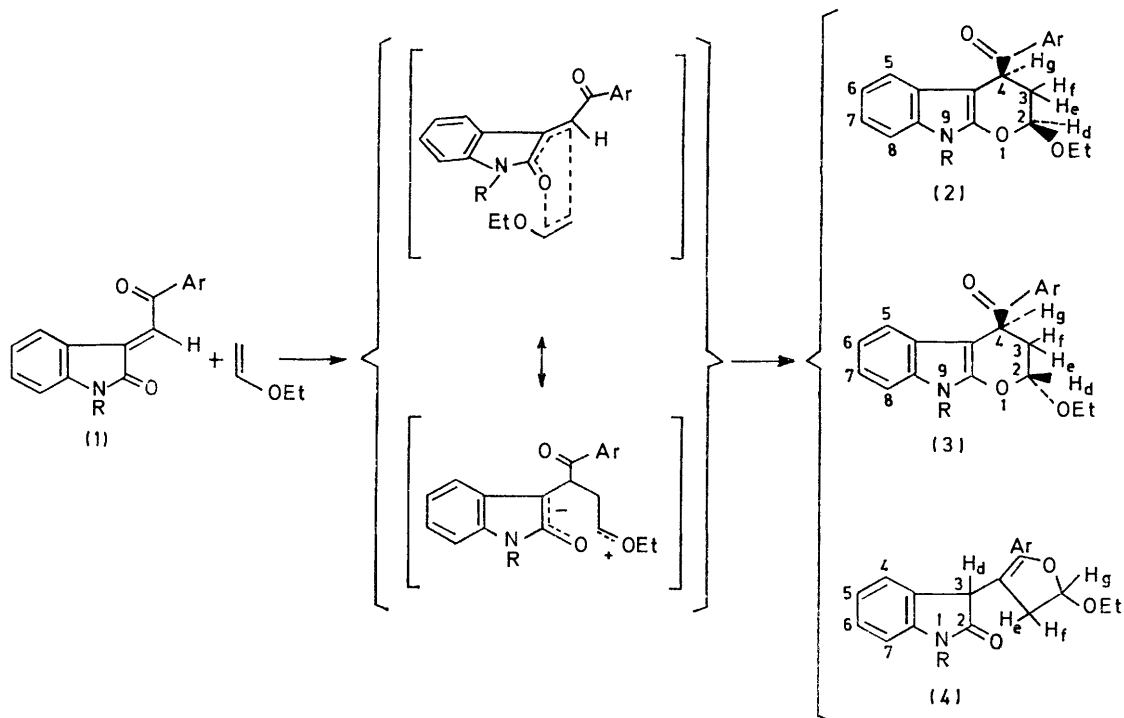
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In addition to dihydropyran[(2) and (3)] and dihydrofuran (4) derivatives, the reaction of (1-acetyl-2-oxoindolin-3-ylidene)acetophenones with ethyl vinyl ether gives 1-acetyl-3-aryl-5-ethoxy-2a,3,4,5-tetrahydrobenz[*cd*]indol-2(1*H*)-ones. Their formation is rationalized in terms of a Diels-Alder reaction between the vinyl ether and the styrenic diene system of the oxoindolylidene derivatives, followed by a hydrogen shift and re-aromatization. The configuration and conformation of the new adducts were determined by n.m.r. spectroscopy and confirmed by X-ray analysis.

We have previously² described the reaction of (*E*)-2-oxoindolin-3-ylideneacetophenones (1)² with ethyl vinyl ether to give *cis*- and *trans*-2,3-dihydropyrano[2,3-*b*]indoles (2) and (3) via a [4 + 2] heterodiene cycloaddition, and 3-(2-oxoindolin-3-yl)dihydrofurans (4), whose formation involves a zwitterionic intermediate (Scheme 1). When the *N*-substituent is an acyl group

RESULTS AND DISCUSSION

The elemental analysis of the colourless by-product is consistent with a 1 : 1 adduct, and the i.r. spectrum still has three carbonyl bands, with the ketonic absorption shifted to higher wave number owing to removal of conjugation (see Experimental section). If the exocyclic C=C group is involved in the reaction, at first glance a



SCHEME 1

all the aryl substrates (1; Ar = Ph, *p*-MeO·C₆H₄, or *p*-NO₂·C₆H₄) gave a low yield of a fourth product; we report here the elucidation of its structure, which helps to clarify the complex mechanism of heterodiene reactions and indicates their synthetic possibilities.

¹ Part XV, G. Desimoni, M. Monticelli, M. Nicola, and G. Tacconi, *J. Amer. Chem. Soc.*, in the press.

² G. Tacconi, P. Iadarola, F. Marinone, P. P. Righetti, and G. Desimoni, *Tetrahedron*, 1975, **31**, 1179.

[2 + 2] cycloaddition to give a spirocyclobutane derivative or a Michael reaction seem the most reasonable pathways since such behaviour has already been found in enamine reactions.³

However, the n.m.r. spectra (Table 8) showed the loss of an aromatic proton from the indoline system. Decoupling experiments (Figure 1) showed the presence of

³ G. Tacconi, A. Gamba, F. Marinone, and G. Desimoni, *Tetrahedron*, 1971, **27**, 561.

the sequence $\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}$. Therefore, a tricyclic structure, formed by a reaction involving both the exocyclic double bond and the 4-position of the indoline is proposed, with the formation of a new type of adduct: a 1-acetyl-3-aryl-5-ethoxy-2a,3,4,5-tetrahydrobenz[*cd*]-indole (5).

the same zwitterionic intermediate already proposed for the formation of (4),² the positive end of which could perform an electrophilic intramolecular attack at the 4-position of the indoline [route (b)]. If pathway (b) were followed, the electrophilic attack would be favoured by an electron-donating group in position 5, whereas an

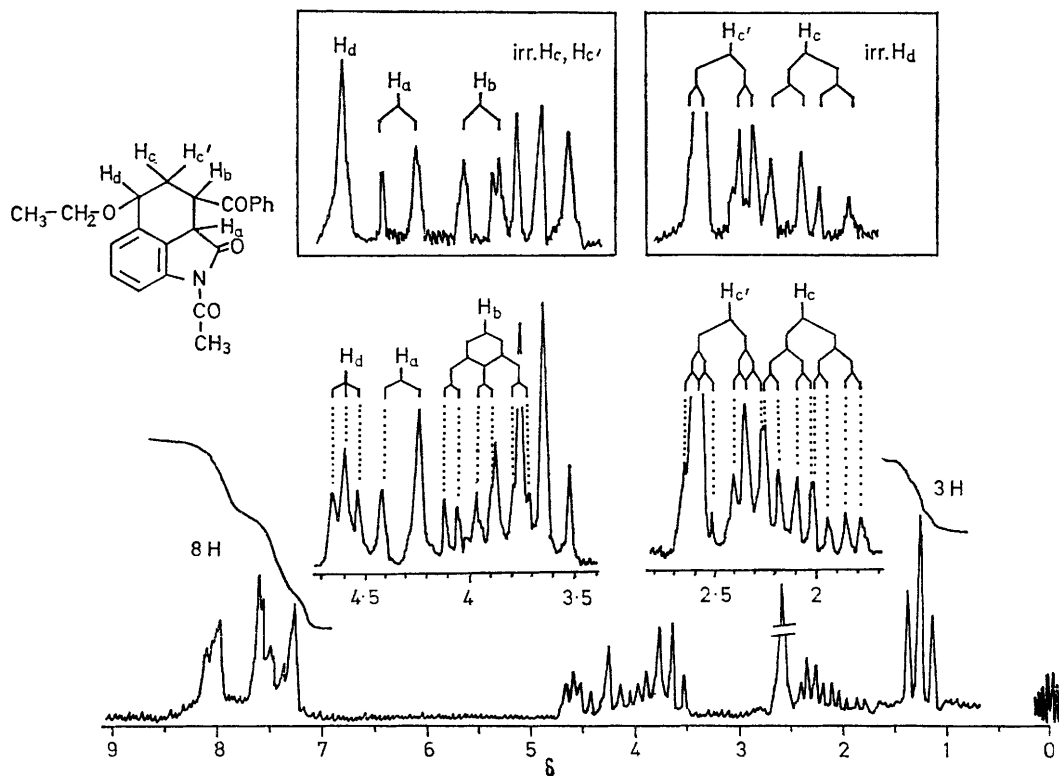
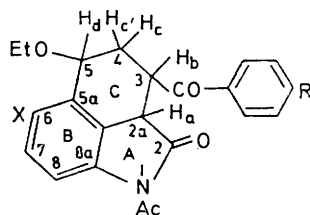
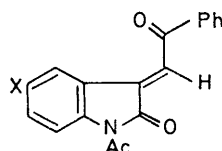


FIGURE 1 N.m.r. spectrum of the adduct (5a)

The question arises as to whether the formation of (5) occurs *via* a Diels–Alder reaction between the vinyl ether



- (5) a; R = X = H
 b; R = OMe, X = H
 c; R = NO₂, X = H
 d; R = H, X = OMe
 e; R = H, X = NO₂



- (6) a; X = OMe
 b; X = NO₂

and the styrene-like fragment, followed by hydrogen transfer and rearomatization [Scheme 2, route (a)] or *via*

⁴ P. Bamfield, A. W. Jonson, and A. F. Katner, *J. Chem. Soc. (C)*, 1966, 1028.

⁵ J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

⁶ J. Sauer, *Angew. Chem. Internat. Edn.*, 1966, **5**, 211.

electron-attracting group should disfavour the reaction. Therefore, the reactions of 1-acetyl-5-methoxy- and 1-acetyl-5-nitro-2-oxindolin-3-ylideneacetophenones (6a and b) with ethyl vinyl ether were studied.

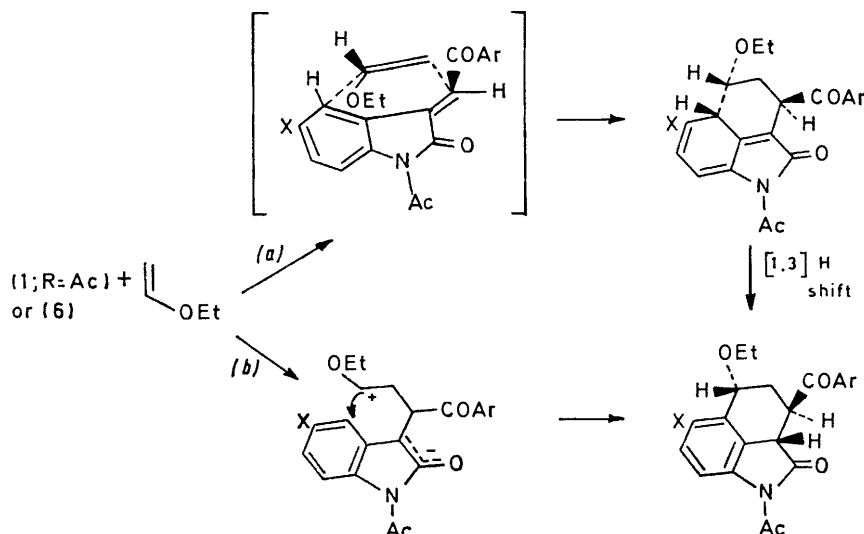
Both substrates gave comparable amounts of the tricyclic adducts (5d and e) as well as the methoxy-analogues of (2)–(4) or the nitro-analogues of (2) and (3), respectively. Since substituents with opposite electronic characters thus show no effect on the formation of the new adduct, a Diels–Alder pathway [Scheme 2, route (a)] is proposed. This reaction mode can be compared with that already found for 2-oxindolin-3-ylideneacetone and acetylenecarboxylates.⁴ If the latter example can be regarded simply as a 'direct' Diels–Alder reaction⁵ between an aromatic diene⁶ and acetylenecarboxylates, which probably act as acceptors,⁷ the reaction mode reported here is unusual, since vinyl ethers usually behave as donors with $\alpha\beta$ -unsaturated carbonyl derivatives.⁸

⁷ (a) R. Sustmann, *Tetrahedron Letters*, 1971, 2721; (b) R. Sustmann and H. Trill, *Angew. Chem. Internat. Edn.*, 1972, **11**, 838; (c) K. N. Houk, *J. Amer. Chem. Soc.*, 1973, **95**, 4092.

⁸ G. Desimoni and G. Tacconi, *Chem. Rev.*, 1975, **75**, 651.

The n.m.r. spectra of the adducts (5) were analysed in detail. The C-2a proton signal appeared as a doublet with a large 2a,3-axial-axial coupling; the aroyl substituent must therefore be in the equatorial position (see Figure 1). The C-5 proton showed two almost equal and small equatorial-equatorial and equatorial-axial

Diels-Alder cycloaddition, since an *endo*-approach is required (Scheme 2) on account of the (*E*)-configuration of the starting material (1).^{3,9} The following step is a rearrangement, driven by the aromaticity gain, of the adduct formed first through a [1,3] suprafacial hydrogen shift; this mode of reaction gives the configuration



SCHEME 2

TABLE 1

Bond lengths (Å; e.s.d. less than 0.005 Å) and bond angles (°; e.s.d. less than 0.5°); figures involving hydrogen atoms are not listed

Distances				Angles			
N(1)-C(2)	1.426	C(7)-C(8)	1.386	C(2)-N(1)-C(8a)	109.1	N(1)-C(8a)-C(8)	131.0
N(1)-C(8a)	1.433	C(8)-C(8a)	1.379	C(2)-N(1)-C(16)	126.3	N(1)-C(8a)-C(8b)	109.1
N(1)-C(16)	1.390	C(8a)-C(8b)	1.385	C(8a)-N(1)-C(16)	124.5	C(8)-C(8a)-C(8b)	119.5
C(2)-C(2a)	1.516	C(9)-C(10)	1.492	N(1)-C(2)-C(2a)	106.5	C(2a)-C(8b)-C(5a)	126.7
C(2)-O(19)	1.202	C(9)-O(25)	1.210	N(1)-C(2)-O(19)	125.9	C(2a)-C(8b)-C(8a)	109.7
C(2a)-C(3)	1.515	C(10)-C(11)	1.373	C(2a)-C(2)-O(19)	127.6	C(5a)-C(8b)-C(8a)	123.1
C(2a)-C(8b)	1.486	C(10)-C(15)	1.398	C(2)-C(2a)-C(3)	121.7	C(3)-C(9)-C(10)	118.0
C(3)-C(4)	1.542	C(11)-C(12)	1.416	C(2)-C(2a)-C(8b)	103.3	C(3)-C(9)-O(25)	121.4
C(3)-C(9)	1.520	C(12)-C(13)	1.365	C(3)-C(2a)-C(8b)	109.5	C(10)-C(9)-O(25)	120.5
C(4)-C(5)	1.537	C(13)-C(14)	1.320	C(2a)-C(3)-C(4)	105.8	C(9)-C(10)-C(11)	124.4
C(5)-C(5a)	1.508	C(14)-C(15)	1.406	C(2a)-C(3)-C(9)	113.5	C(9)-C(10)-C(15)	118.2
C(5)-O(22)	1.432	C(16)-O(17)	1.211	C(4)-C(3)-C(9)	107.5	C(11)-C(10)-C(15)	117.3
C(5a)-C(6)	1.405	C(16)-C(18)	1.491	C(3)-C(4)-C(5)	113.1	C(10)-C(11)-C(12)	120.9
C(5a)-C(8b)	1.359	O(20)-C(21)	1.415	C(4)-C(5)-C(5a)	112.7	C(11)-C(12)-C(13)	119.5
C(6)-C(7)	1.381	O(22)-C(23)	1.423	C(4)-C(5)-O(22)	108.3	C(12)-C(13)-C(14)	120.9
C(6)-O(20)	1.370	C(23)-C(24)	1.492	C(5a)-C(5)-O(22)	106.7	C(13)-C(14)-C(15)	120.8
				C(5)-C(5a)-C(6)	123.8	C(10)-C(15)-C(14)	120.5
				C(5)-C(5a)-C(8b)	118.9	N(1)-C(16)-O(17)	119.8
				C(6)-C(5a)-C(8b)	117.0	N(1)-C(16)-C(18)	118.3
				C(5a)-C(6)-C(7)	120.5	O(17)-C(16)-C(18)	121.9
				C(5a)-C(6)-O(20)	113.5	C(6)-O(20)-C(21)	119.0
				C(7)-C(6)-O(20)	126.0	C(5)-O(22)-C(23)	113.3
				C(6)-C(7)-C(8)	121.0	O(22)-C(23)-C(24)	109.5
				C(7)-C(8)-C(8a)	118.5		

couplings with the C-4 protons, the latter axial one also being coupled (axial-axial) with the C-3 proton. Therefore the 5-ethoxy-group is axial and *trans* to the aroyl substituent.

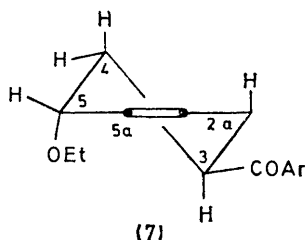
The preferred conformation of the cyclohexene ring (c) is thus represented as in (7). The *trans*-OEt,COAr configuration allows us to infer the transition state of the

actually found in (5). However, a [1,5] shift followed by keto-enol tautomerization or anionic proton loss and gain cannot *a priori* be excluded, but it seems unlikely that a single isomer would be obtained.

Because of the importance of the configuration of the tricyclic adduct in defining the mechanism, the deduc-

• R. L. Autrey and F. C. Tahk, *Tetrahedron*, 1967, **23**, 901.

tions from n.m.r. data were confirmed by an X-ray analysis of the methoxy-derivative (5d) (Figure 2).



Crystal Structure.*—The crystal structure refinement yielded a final conventional *R* factor of 3.6%. The

TABLE 2

Torsion angles (°); only the most significant are reported; e.s.d. range 0.3–0.7°; A and c denote the internal torsion angles of the corresponding rings; B denotes torsion angles involving relationships between ring b and a and/or c

A	C(8a)–N(1)–C(2)–C(2a)	167.1
	C(8a)–N(1)–C(2)–O(19)	–11.1
	C(16)–N(1)–C(2)–C(2a)	–16.3
	C(16)–N(1)–C(2)–O(19)	165.5
	C(2)–N(1)–C(8a)–C(8)	12.4
A	C(2)–N(1)–C(8a)–C(8b)	–174.9
	C(16)–N(1)–C(8a)–C(8)	–164.2
	C(16)–N(1)–C(8a)–C(8b)	8.5
	C(2)–N(1)–C(16)–O(17)	4.0
	C(2)–N(1)–C(16)–C(18)	–175.5
	C(8a)–N(1)–C(16)–O(17)	–179.9
	C(8a)–N(1)–C(16)–C(18)	0.6
	N(1)–C(2)–C(2a)–C(3)	–41.4
A	N(1)–C(2)–C(2a)–C(8b)	–164.8
	O(19)–C(2)–C(2a)–C(3)	136.8
	O(19)–C(2)–C(2a)–C(8b)	13.4
	C(2)–C(2a)–C(3)–C(4)	4.3
	C(2)–C(2a)–C(3)–C(9)	–113.3
C	C(8b)–C(2a)–C(3)–C(4)	124.8
	C(8b)–C(2a)–C(3)–C(9)	7.1
	C(2)–C(2a)–C(8b)–C(5a)	–19.9
A	C(2)–C(2a)–C(8b)–C(8a)	167.4
C	C(3)–C(2a)–C(8b)–C(5a)	–151.1
	C(3)–C(2a)–C(8b)–C(8a)	36.3
C	C(2a)–C(3)–C(4)–C(5)	–115.6
	C(9)–C(3)–C(4)–C(5)	6.0
	C(2a)–C(3)–C(9)–C(10)	22.8
	C(2a)–C(3)–C(9)–O(25)	–153.4
	C(4)–C(3)–C(9)–C(10)	–93.8
	C(4)–C(3)–C(9)–O(25)	89.9
C	C(3)–C(4)–C(5)–C(5a)	139.4
	C(3)–C(4)–C(5)–C(22)	–102.8
	C(4)–C(5)–C(5a)–C(6)	3.0
C	C(4)–C(5)–C(5a)–C(8b)	–170.5
	O(22)–C(5)–C(5a)–C(6)	–115.8
	O(22)–C(5)–C(5a)–C(8b)	70.7
	C(4)–C(5)–O(22)–C(23)	–83.3
	C(5a)–C(5)–O(22)–C(23)	38.4
	C(5)–C(5a)–C(6)–C(7)	8.6
	C(5)–C(5a)–C(6)–O(20)	–171.7
BC	C(5)–C(5a)–C(8b)–C(2a)	175.7
B	C(5)–C(5a)–C(8b)–C(8a)	–12.6
	C(5a)–C(6)–O(20)–C(21)	1.4
	C(7)–C(6)–O(20)–C(21)	–178.9
AB	N(1)–C(8a)–C(8b)–C(2a)	–174.8
B	N(1)–C(8a)–C(8b)–C(5a)	12.2
B	C(8)–C(8a)–C(8b)–C(2a)	–1.2
	C(3)–C(9)–C(10)–C(11)	–174.2
	C(3)–C(9)–C(10)–C(15)	8.3
	O(25)–C(9)–C(10)–C(11)	2.1
	O(25)–C(9)–C(10)–C(15)	–175.4
	C(5)–O(22)–C(23)–C(24)	4.7

results of the anisotropic refinement (see Experimental section) are shown in Figure 2, which depicts the 25%

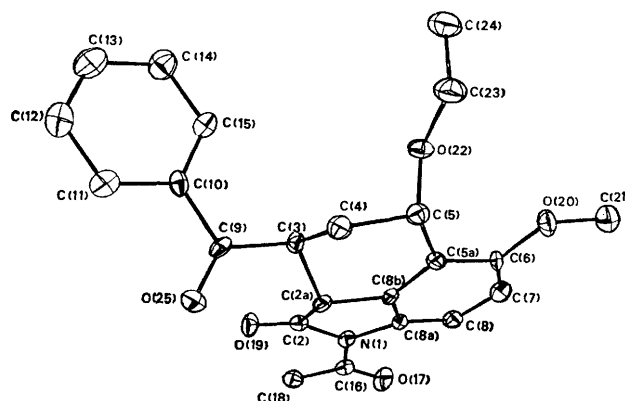


FIGURE 2 ORTEP view of the molecular skeleton of the adduct (5d) (hydrogen atoms not included); the thermal ellipsoids are depicted according to the output of the last least-squares cycle (see text)

probability ellipsoids.¹⁰ Bond lengths and angles not involving hydrogen atoms are listed in Table 1, and the more significant torsion angles are given in Table 2. An analysis of the planarity of the ring is provided in Table 3. Tables of structure factors, atomic fractional co-

TABLE 3

Distances (Å) of the ring atoms from their least-squares interpolating planes; arranged in the same order as the defining atoms; e.s.d.s less than 0.006 Å

Ring A	N(1)	C(2)	C(2a)	C(8a)	C(8b)	
	+0.046	–0.099	+0.074	–0.007	–0.065	
Ring B	C(5a)	C(6)	C(7)	C(8)	C(8a)	C(8b)
	–0.023	–0.004	+0.026	–0.013	–0.016	+0.037
Ring c	C(2a)	C(3)	C(4)	C(5)	C(5a)	C(8b)
	+0.240	–0.349	+0.296	–0.080	–0.095	+0.014
Ph of	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)
PhCO	–0.003	+0.003	–0.001	0	0	+0.001

ordinates, and thermal parameters are listed in Supplementary Publication No. SUP 21741 (12 pp., 1 microfiche).†

Both Tables 2 and 3 clearly show the half-chair conformation of ring c (in Table 2 the appropriate internal torsion angles are labelled c). The phenyl ring of the benzoyl group is strictly planar (Table 4). The distortion of the aromatic ring b from planarity (see also Table 3) is clearly connected with its fusion with the non-planar system ac. The angles between pairs of rings of the fused system are AB, 10.3°; AC, 13.0°; BC, 11.7°.

The final distances range between 0.88 and 1.16 Å, with fairly good angles. The shortest intermolecular distances are listed in Table 4; some are remarkably

* Work carried out at the Centro di Studio per la Cristallografia stuttarale del C.N.R., Pavia.

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

¹⁰ C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report ORNL-3794, 1965.

short and apparently relatively strong molecular interactions are involved.

It is unfortunate that these new adducts are formed in such low yields because, in addition to their theoretical

TABLE 4

Shortest intermolecular distances (Å); e.s.d.s less than 0.005 Å

Symmetry code:

(i) $x, 1 + y, z$	(vi) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$		
(ii) $-x, 1 - y, 1 - z$	(vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$		
(iii) $-x, 1 - y, 2 - z$	(viii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$		
(iv) $-x, 2 - y, 1 - z$	(ix) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$		
(v) $-x, 2 - y, 2 - z$			
N(1) ... O(25 ^v)	3.062	C(18) ... H3(24 ⁱ)	2.991
C(2) ... O(25 ^v)	3.066	O(19) ... H2(21 ^{vi})	2.706
C(2a) ... O(25 ^v)	3.290	C(21) ... H2(24 ⁱⁱ)	2.895
C(15) ... H3(24 ⁱⁱⁱ)	3.036	O(22) ... H1(18 ^{viii})	2.762
O(17) ... H(7 ^{iv})	2.842	O(25) ... H(2a ^v)	2.672
O(17) ... H(11 ^{vii})	2.807	O(25) ... H(13 ^{ix})	2.745
O(17) ... H3(21 ^{iv})	2.577	H1(4) ... H1(23 ⁱⁱⁱ)	2.479
C(18) ... O(22 ^{viii})	3.209	H2(18) ... H3(24 ⁱ)	2.641

interest, they could provide a potential synthetic approach to ergot-type precursors.

EXPERIMENTAL

I.r. spectra (Nujol mulls) were obtained with a Perkin-Elmer 257 spectrophotometer. N.m.r. data were obtained

(from dioxan) (Found: C, 65.5; H, 3.5; N, 9.7. $C_{16}H_{10}N_2O_4$ requires C, 65.3; H, 3.45; N, 9.5%).

(1-Acetyl-2-oxoindolin-3-ylidene)acetophenones (1; R = Ac).—These were prepared by acetylation of the 1-unsubstituted derivatives by the literature methods: (1-acetyl-2-oxoindolin-3-ylidene)acetophenone (Ar = Ph),¹⁴ (1-acetyl-2-oxoindolin-3-ylidene)-*p*-methoxyacetophenone (Ar = *p*-MeO-C₆H₄),² (1-acetyl-2-oxoindolin-3-ylidene)-*p*-nitroacetophenone (Ar = *p*-NO₂-C₆H₄).²

(1-Acetyl-5-methoxy-2-oxoindolin-3-ylidene)acetophenone (6a). This was obtained (45%) as red-violet needles, m.p. 147° (from acetic acid) (Found: C, 71.2; H, 4.8; N, 4.4. $C_{19}H_{15}NO_4$ requires C, 71.0; H, 4.7; N, 4.35%), ν_{max} 1 745s, 1 709s, 1 659s, and 1 620w cm⁻¹ (C=O of lactam, acetyl, and ketone, and exocyclic C=C, respectively), insufficiently soluble for n.m.r. data to be obtained.

(1-Acetyl-5-nitro-2-oxoindolin-3-ylidene)acetophenone (6b). This was obtained (77%) as yellow crystals, m.p. 204—205° (from acetic acid) (Found: C, 64.4; H, 3.7; N, 8.5. $C_{18}H_{12}N_2O_5$ requires C, 64.3; H, 3.6; N, 8.35%), ν_{max} 1 753s, 1 722s, 1 669s, and 1 622w cm⁻¹ (C=O of lactam, acetyl, and ketone, and exocyclic C=C, respectively), δ 8.06 (s, vinylic H).

Reaction of the Indolylideneacetophenones with Ethyl Vinyl Ether.—General method. As in the previously reported method,² a suspension of the substrate [(1) or (6)] (4 mmol) in ethyl vinyl ether (12 ml) was heated at 100 °C in a Paar apparatus [reaction times 1 and 1.5 h for (6a) and (6b) respectively]. After cooling pure or nearly pure adduct of

TABLE 5

Properties of dihydropyran- and dihydrofuran-type adducts

Compd.	Physical aspect [yield (%)]	M.p. (°C)	Elemental analysis (%)	I.r. (ν/cm^{-1})		
				ν (C=O) (acetyl)	ν (C=O) (lactam)	ν (C=O) (ketone)
(2; Ar = Ph; 6-OMe)	Soft white needles [72]	158—160 ^a	Found: C, 69.9; H, 5.9; N, 3.7	1 712s	Absent	1 689s
(3; Ar = Ph; 6-OMe)	Small yellowish crystals [8]	146—147 ^a	Found: C, 70.55; H, 6.05; N, 3.7	1 703s	Absent	1 672s
(4; Ar = Ph; 5-OMe)	White platelets [4]	111—113 ^b	Found: C, 70.3; H, 6.0; N, 3.65 $C_{23}H_{23}NO_5$ requires C, 70.2; H, 5.9; N, 3.55	1 700s	1 756s	Absent
(2; Ar = Ph; 6-NO ₂)	Soft pale yellow needles [70]	154—155 ^c	Found: C, 64.8; H, 5.0; N, 6.9	1 715s	Absent	1 686s
(3; Ar = Ph; 6-NO ₂)	Soft pale yellow needles [12]	159—160 ^c	Found: C, 64.85; H, 5.1; N, 6.95 $C_{22}H_{20}N_2O_6$ requires C, 64.7; H, 4.95; N, 6.85	1 716s	Absent	1 683s

^a From ethanol. ^b From light petroleum. ^c From benzene.

by Dr. A. G. Invernizzi with a Perkin-Elmer R12A spectrophotometer (solvent, unless otherwise stated, CDCl₃). Microanalyses were performed by Dr. D. Maggi.

(2-Oxoindolin-3-ylidene)acetophenones.—The following compounds were prepared by literature methods: (2-oxoindolin-3-ylidene)acetophenone,¹¹ *p*-methoxy-(2-oxoindolin-3-ylidene)acetophenone,¹¹ (2-oxoindolin-3-ylidene)-*p*-nitroacetophenone,² and (5-methoxy-2-oxoindolin-3-ylidene)acetophenone.¹²

(5-Nitro-2-oxoindolin-3-ylidene)acetophenone. This was obtained from 5-nitroisatin¹³ and acetophenone by the reported method¹¹ as yellow crystals (53%), m.p. 229—231°

¹¹ H. G. Lindwall and J. S. MacLennan, *J. Chem. Soc.*, 1932, 54, 4739.

¹² S. Pietra and G. Tacconi, *Il Farmaco, Ed. Sci.*, 1958, 13, 893.

type (2) was collected and washed with diethyl ether. Crystalline mixtures of dihydropyrans of types (2) and (3) and benzindolones (5) were obtained as further crops from the concentrated mother liquors, after storage at low temperature. Finally, the oily residue was chromatographed [Merck Kieselgel (0.06—0.2 mm); cyclohexane-ethyl acetate (70 : 30) as eluant] to give pure adduct of type (4) (first fraction) and small amounts of mixtures of adducts of types (2) and (3) and, sometimes, (5). Pure samples were obtained by fractional crystallization from ethanol. All adducts not previously described are reported in Tables 5

¹³ N. O. Calvery, C. R. Noller, and R. Adams, *J. Amer. Chem. Soc.*, 1925, 47, 3059.

¹⁴ T. Kato, H. Yamanaka, and H. Ichikawa, *Chem. and Pharm. Bull. (Japan)*, 1969, 17, 481.

and 6 and the n.m.r. spectra are summarized in Tables 7 and 8.

X-Ray Analysis.—*Crystal data.* $C_{23}H_{23}NO_5$, $M = 393.443$. Monoclinic, space group $P2_1/n$, $a = 12.557(4)$, $b = 12.734(4)$, $c = 12.510(4)$ Å, $\beta = 92.28(4)^\circ$, $U = 1998.779$ Å³, $Z = 4$, $D_c = 1.307$ g cm⁻³, $F(000) = Cu-K\alpha$ radiation, $\lambda = 1.5418$ Å, graphite monochromator, $\mu(Cu-K\alpha) = 7.66$ cm⁻¹.

The cell parameters were determined by scanning rows (h00), (0k0), (00l), (h0h), and ($\bar{h}0h$) on a diffractometer, with Cu-K α radiation up to 50°, and with both positive and

Structure determination and refinement. The structure was solved by direct methods, after application of MULTAN;¹⁵ the solution was obtained with the set of signs with maximum likelihood. Refinement of the starting coordinates was carried out by full-matrix least-squares, until convergence, with a locally modified version of ORFLS¹⁶ (scattering factors¹⁷). No weighting scheme was applied. In the last least-squares cycle the secondary extinction coefficient and the anisotropic thermal parameters of the non-hydrogen atoms were refined, in order to improve the positional co-ordinates; no particular physical meaning is

TABLE 6
Properties of benz[*cd*]indolones (5)

Compd.	Physical aspect [yield (%)]	M.p. (°C)	Elemental analysis (%)		I.r. (ν/cm^{-1})		
					ν (C=O) (acetyl)	ν (C=O) (lactam)	ν (C=O) (ketone)
(5a)	Soft white needles [3—4]	166—167 ^a	Found: $C_{22}H_{21}NO_4$ requires	C, 72.8; H, 5.8; N, 3.9 C, 72.7; H, 5.8; N, 3.85	1702s	1769s	1689s
(5b)	Soft white needles [2—3]	161—162 ^a	Found: $C_{23}H_{23}NO_5$ requires	C, 70.35; H, 6.0; N, 3.6 C, 70.2; H, 5.9; N, 3.55	1709s	1765s	1670s
(5c)	Yellowish needles [4]	181—182 ^a	Found: $C_{22}H_{20}N_2O_5$ requires	C, 65.0; H, 5.05; N, 7.0 C, 64.7; H, 4.95; N, 6.85	1698s	1781s	1684s
(5d)	Pale yellow crystals [2—3]	209—211 ^b	Found: $C_{23}H_{23}NO_5$ requires	C, 70.55; H, 5.95; N, 3.7 C, 70.2; H, 5.9; N, 3.55	1695s	1763s	1678s
(5e)	Small white needles [2—3]	181 ^a	Found: $C_{22}H_{20}N_2O_6$ requires	C, 64.95; H, 4.95; N, 7.0 C, 64.7; H, 4.95; N, 6.85	1710s	1782s	1680s

^a From ethanol. ^b From dioxan.

TABLE 7
N.m.r. data for adducts of types (2)—(4) [Et groups designated $CH_aH_bC(H_c)_3$; for H_{d-g} see formulae]

Compd.	Chemical shifts (δ)									Coupling constants (Hz)			
	H_d	H_e, H_f	H_g	H_a	H_b	H_c	OMe	Ac	ArH	$J_{de} + J_{df}$	$J_{eg} + J_{fg}$	$-J_{ab}$	J_c (<i>vic</i>)
(2; Ar = Ph; 6-OMe)	5.37	2.5	4.57	3.80	3.52	1.16	3.66	2.60	6.4—8.4	7.9	13.5	9.4	7.1
(3; Ar = Ph; 6-OMe)	5.62	2.3	4.95	3.96	3.73	1.25	3.57	2.63	6.25—8.4	7.3	14.5	10.6	7.0
(2; Ar = Ph; 6-NO ₂)	5.47	2.5	4.63	3.89	3.60	1.13		2.67	7.3—8.6	6.6	12.2	9.3	7.3
(3; Ar = Ph; 6-NO ₂)	5.63	2.3	5.01	3.99	3.79	1.28		2.70	7.5—8.6	6.7	14.5	9.4	7.3
(4; Ar = Ph; 5-OMe)	4.79	2.5	5.57	3.96	3.62	1.22	3.75	2.66	6.65—8.25		9.8	9.8	7.2

TABLE 8
N.m.r. data for the adducts (5) [Et designated $C(H_B)_3C(H_A)_2$; for H_{a-d} see formula (5)]

Compd.	Chemical shifts (δ)										Coupling constants (Hz)						
	H_a	H_b	H_c	H_e'	H_d	H_A	H_B	Ac	OMe	ArH	J_{ab}	J_{bc}	$J_{be'}$	J_{ed}	J_{cd}	$-J_{ce'}$	J_{AB}
(5a)	4.29	3.94	2.05	2.40	4.59	3.68	1.24	2.55		7.2—8.3	10.0	10.0	4.0	4.0	4.0	14.0	7.0
(5b)	4.30	3.88	2.05	2.39	4.58	3.82	1.25	2.55	3.87	6.8—8.4	10.0	9.3	4.3	4.3	3.4	14.7	6.7
(5c)	4.26	3.96	2.09	2.42	4.64	3.72	1.26	2.55		7.15—8.5	10.5	9.9	3.9	4.3	3.3	14.2	6.8
(5d)	4.29	3.85	1.88	2.51	4.74	3.75	1.22	2.54	3.88	6.7—8.25	10.6	10.6	2.7	2.7	2.7	14.5	7.0
(5e)	4.36	3.96	1.97	2.25	5.41*	3.67	1.14	2.58		7.4—8.3	10.6	10.7	3.6	4.0	2.0	14.7	7.1

* Equatorial proton deshielded by NO₂.

negative θ values for assessing the zero of the corresponding circle.

Intensity measurements. 1302 reflections with θ ($Cu-K$) $\leq 40^\circ$ were collected with a Philips PW1100 automatic diffractometer (from a crystal of approximately cubic shape and dimensions: $0.032 \times 0.035 \times 0.038$ cm); the working conditions were as follows: ω -2 θ scan mode, ω range 1.4° , scan speed 0.05° s⁻¹; 0.06° of background radiation was measured on each side of the peak. The 1127 reflections with $I < 3\sigma$ (I) were considered unobservably weak. Three reference reflections were monitored every 2 h and no decomposition was observed. The intensities were not corrected for absorption.

¹⁵ P. Main, M. M. Woolfson, and G. Germain, 'MULTAN—a Computer Program for the Automatic Solution of Crystal Structures,' Universities of York, England, and Leuven, Belgium, 1971.

claimed for individual B_{ij} values, and accordingly they are not reported.

All the hydrogen atoms were found as the more prominent peaks in a ($F_o - F_c$) Fourier synthesis; they were refined isotropically.

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¹⁶ W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratory Report ORNL-TM-305, 1962.

¹⁷ H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.