Heterodiene Syntheses. Part 21.[1] 1-Acetyl-2-oxoindolin-3-ylideneacetophenones and Ethoxyethyne: Spirobicyclic Intermediates in Competition with [2 + 2]- and [4 + 2]-Cycloadditions

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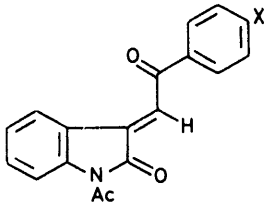
1-Acetyl-2-oxo-1*H*-indolin-3-ylideneacetophenones (1) react with ethoxyethyne (2) to give colourless pyrano-[2,3-*b*]indoles (3), in accordance with a (1,4) cycloaddition, and coloured 3-propenylideneindolin-2-ones. The latter are formed by a (1,2) cycloaddition followed by electrocyclic ring opening of the spirocyclobutene intermediate to the unsaturated ketone (5) or by rearrangement of two spirobicyclic intermediates which undergo ring opening to give the unsaturated esters (6) and (7). Adducts (3), (6), and (7) are stereochemically correlated through a stable isomer (8) whose (*E,E*)-configuration was confirmed by *X*-ray analysis. The mechanism of formation of the various adducts is discussed.

In the previous part of this series[1] we discussed the reaction of 4-arylidenepyrazol-5-ones with *NN*-diethylaminomethylacetylene to give [4 + 2]- and [2 + 2]-cycloadducts, the latter of which rearrange to open-chain unsaturated derivatives. A zwitterionic intermediate was suggested for both adducts.

4-Arylidenepyrazol-5-ones react with alkoxyacetylenes to give (1,4) cycloadducts only[2,3] and this can be rationalized in terms of lower highest-occupied molecular orbital energy for acetylenic ethers compared with those of ynamine.[4]

In this paper we discuss the behaviour of the heterodiene reactions with acetylenic ethers if the heterocyclic



(1) a; X = NO_2
b; X = Br
c; X = H
d; X = OMe

(2)

αβ-unsaturated carbonyl substrate has an electron-attracting β-substituent which lowers the lowest unoccupied molecular orbital (LUMO) energy and therefore diminishes the frontier-orbital energy separation of the reagents. We examined the reaction of 1-acetyl-2-oxo-1*H*-indolin-3-ylideneacetophenones (1a—d) with ethoxyethyne (2).

RESULTS

The reactions were performed in benzene at room temperature and required a few days for completion. T.l.c. showed the presence in the reaction mixture of at least four different products, which could be separated by using their different solubilities in diethyl ether (see Experimental section for details).

The major products (3a—d) are colourless crystalline solids, whose i.r. spectra show the absence of both the lactam CO band and the conjugated ketonic ν_{CO} (in the range 1 680—1 690 cm^{-1}). The n.m.r. spectra (Table 1) are consistent with 2-ethoxy-4-aroyl-9-acetylpyrano[2,3-*b*]indoles and the previously described[5] catalytic reduction of (3c) to the *cis*-dihydropyrano[2,3-*b*]indole, further supports this assumption.

In general three other adducts, all yellow to orange, are formed in varying yields and their n.m.r. spectra (Table 2) show the presence of a –C=C– fragment with a *trans* coupling for the lowest yield isomer and a *cis* coupling for the others. The former, which were formed in ⩽3% yields, have i.r. spectra (Table 3; lactam ν_{CO} lowered by conjugation with the ethoxy-group, and a conjugated ketonic ν_{CO} and n.m.r. spectra (Table 2; chemical shift of the olefinic protons) consistent with their formulation as 1-acetyl-3-(1-ethoxy-3-aroylpropenylidene)indolin-2-ones (5a—d).

The (3*Z*,2'*E*) configuration was assigned to compounds (5) because the 2'-proton was not deshielded (see later) and from mechanistic considerations of their origin.[1] It is evident that compounds (5) are formed by conrotatory electrocyclic opening of the spiro-cyclobutenes (4), which

TABLE 1

N.m.r. data for the pyrano[2,3-*b*]indoles (3). The Et group is designated $C(H_A)_2C(H_B)_3$

	Chemical shifts (δ)							Coupling constants/Hz	
Compound	H-3	H-4	H_A	H_B	Ac	OMe	Ar-H	*J*(3,4)	*J*(A,B)
(3a)	5.22 (d)	4.21 (d)	3.95 (q)	1.35 (t)	2.71 (s)		7.0—8.5 (m)	3.6	6.9
(3b)	5.13 (d)	4.14 (d)	3.91 (q)	1.33 (t)	2.69 (s)		6.9—8.6 (m)	3.6	6.9
(3c) *	5.25 (d)	4.18 (d)	3.88 (q)	1.30 (t)	2.70 (s)		6.8—8.5 (m)	3.8	7.0
(3d)	5.18 (d)	4.18 (d)	3.90 (q)	1.31 (t)	2.68 (d)	3.84 (s)	6.8—8.5 (m)	3.6	7.0

* Values taken from ref. 5.

TABLE 2

N.m.r. data for the 3-propenylideneindolin-2-ones (5—8). The Et group is designated $C(H_A)_2C(H_B)_3$

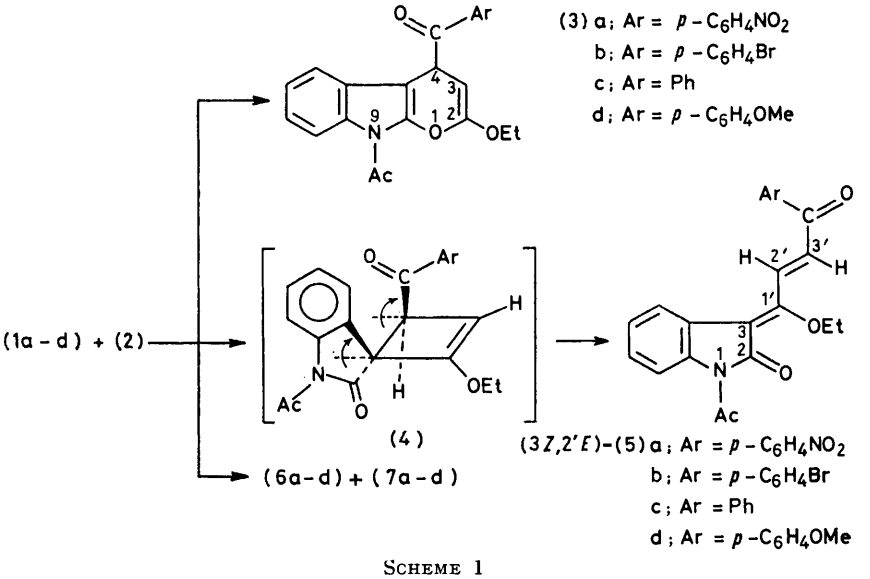
Compound	Chemical shifts (δ) H-2′	H-3′	H_A	H_B	Ac	OMe	Ar-H	Coupling constants/Hz $J(2',3')$	$J(A,B)$
(5a)	8.55 (d)	7.43 (d)	4.24 (q)	1.54 (t)	2.70 (s)		7.1—8.5 (m)	15.7	6.9
(5b)	8.50 (d)	7.44 (d)	4.24 (q)	1.53 (t)	2.71 (s)		7.0—8.3 (m)	15.8	7.1
(5c) [a]	8.51 (d)	7.53 (d)	4.23 (q)	1.53 (t)	2.69 (s)		7.0—8.3 (m)	15.9	6.9
(5d)	8.46 (d)	7.52 (d)	4.24 (q)	1.51 (t)	2.69 (s)	3.88 (s)	6.8—8.4 (m)	15.8	6.9
(6a)	7.59 (d)	6.22 (d)	3.87 (q)	1.09 (t)	2.72 (s)		6.3—8.5 (m)	12.3	6.9
(6b)	7.54 (d)	6.18 (d)	3.85 (q)	1.09 (t)	2.73 (s)		6.5—8.4 (m)	12.1	6.9
(6c)	7.57 (d)	6.15 (d)	3.77 (q)	1.05 (t)	2.70 (s)		6.3—8.4 (m)	12.0	6.9
(6d)	7.51 (d)	6.17 (d)	3.80 (q)	1.04 (t)	2.71 (s)	3.85 (s)	6.3—8.4 (m)	12.0	7.1
(7a)	7.18 (d)	6.33 (d)	3.90 (q)	1.05 (t)	2.55 (s)		7.0—8.5 (m)	12.0	7.0
(7b)	7.16 (d)	6.30 (d)	3.88 (q)	1.06 (t)	2.59 (s)		7.0—8.5 (m)	12.0	6.9
(7c)	7.17 (d)	6.27 (d)	3.82 (q)	1.03 (t)	2.58 (s)		7.0—8.5 (m)	12.0	6.9
(7d)	7.14 (d)	6.28 (d)	3.80 (q)	1.02 (t)	2.59 (s)	3.81 (s)	6.8—8.5 (m)	12.0	7.0
(8a)	9.38 (d)	5.61 (d)	4.24 (q)	1.29 (t)	2.75 (s)		5.8—8.6 (m)	15.9	7.0
(8b) [b]	9.33 (d)	5.71 (d)	4.24 (q)	1.28 (t)	2.75 (s)		5.9—8.6 (m)	15.7	7.1
(8c) [b]	9.38 (d)	5.76 (d)	4.24 (q)	1.28 (t)	2.75 (s)		5.8—8.4 (m)	15.8	7.0
(8d) [b]	9.29 (d)	5.79 (d)	4.23 (q)	1.28 (t)	2.74 (s)	3.91 (s)	6.0—8.4 (m)	15.8	7.0

[a] Signals determined in a mixture with (7c). [b] Obtained by isomerization of the corresponding (3), (6), or (7).

are the primary products from a [2 + 2]cycloaddition to the exocyclic C=C bond of (1) (Scheme 1).

The coloured adducts (6) and (7) have i.r. spectra with no ν_{CO} band $<1\,700$ cm^{-1} (Table 3), which indicates the absence of the fragment Ar–CO–CH=CH; the similarity in shape of the carbonyl region with that of 2-oxindolin-3-ylidene acetates [6] suggests the presence of an unsaturated ester group in (6) and (7). Since both give the same acid on acid hydrolysis (see later), they must be stereoisomers.

Except for compounds (5), which are stable, all the other adducts can be correlated since in polar solvents, acid conditions, or by heating, they all rearrange to new stable isomers (8a—d) which are coloured unsaturated esters with a *trans*-ethylenic fragment. The chemical shift of H-2′ at extremely low field (see Table 3) allows assignment of the (*E*,*E*)-configuration to (8a—d) and therefore also to the acid (9) which is obtained from (8c), (6c), and (7c) upon heating



SCHEME 1

Their structure was inferred by n.m.r. which shows (*a*) an ethoxy-group; (*b*) a *cis*-coupling of the protons of the ethylenic fragment; (*c*) olefinic protons which have chemical shifts consistent with a conjugated structure; and (*d*) the absence of a 1′-ethoxycarbonyl group since, in the *E*-configuration (and therefore in at least one stereoisomer), this causes a strong deshielding of the indolinone H-4,[7,8] and this was not seen in the spectra of (6) and (7).

From the above considerations, and from the deshielding of H-2′ in (6) due to the proximity to the carbonyl lactam, the structures (3*E*,2′*Z*)- and (3*Z*,2′*Z*)-1-acetyl-3-(1-aryl-3-ethoxycarbonylpropenylidene)indolin-2-one were proposed for (6) and (7) respectively.

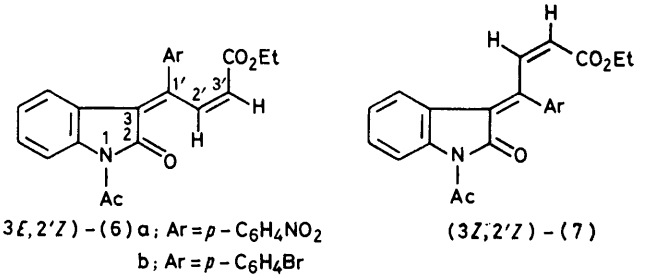


TABLE 3

Preparation, i.r. spectra, and analytical data of adducts (3) and (5—8)

Compound	Yield (%)	Type of separation [a]	M.p. (°C) [b]	Elemental analyses (%)	ν_{CO}/cm^{-1}
(3a)	55	*A*	191—192 [c]	Found: C, 65.0; H, 4.65; N, 6.8	1 705, 1 690
(5a)	3	*B*	189—190 [d]	Found: C, 64.75; H, 4.5; N, 6.95	1 705, 1 663
(6a)	12	*B*	155—160 [d]	Found: C, 65.0; H, 4.5; N, 6.9	1 730, 1 710
(7a)	9	*B*	147—148 [d]	Found: C, 65.1; H, 4.65; N, 7.0	1 735, 1 710
(8a)	12	*B*	194—195 [d]	Found: C, 65.15; H, 4.5; N, 7.0	1 740, 1 710
				($C_{22}H_{18}N_2O_6$ requires C, 65.0; H, 4.45; N, 6.9)	
(3b)	48	*A*	177—178 [c]	Found: C, 59.75; H, 4.2; N, 3.25; Br, 18.25	1 705, 1 680
(5b)	2	*D* + *C*	177—178 [d]	Found: C, 59.85; H, 4.2; N, 3.25; Br, 18.3	1 710, 1 655
(6b)	27	*C* + *D*	131—132 [d]	Found: C, 60.25; H, 4.2; N, 3.2; Br, 18.1	1 733, 1 715
(7b)	6	*D* + *C*	100—101 [d]	Found: C, 60.25; H, 4.2; N, 3.2; Br, 18.1	1 740, 1 720, 1 703
(8b)			179—180 [d]	Found: C, 59.9; H, 4.15; N, 3.2; Br, 18.3	1 730, 1 700
				($C_{22}H_{19}BrNO_4$ requires C, 60.0; H, 4.1; N, 3.2; Br, 18.15)	
(3c)	47	*A*	183—185 [f]	Found: C, 73.25; H, 5.3; N, 4.0	1 720, 1 685
(6c)	25	*C* + *E*	113—114 [d]	Found: C, 72.95; H, 5.3; N, 4.05	1 730, 1 718, 1 700
(7c)	9	*E*	156—157 [d]	Found: C, 73.3; H, 5.2; N, 3.85	1 735, 1 700
(8c)			174—175 [d]	Found: C, 73.35; H, 5.4; N, 4.15	1 740, 1 713
				($C_{22}H_{19}NO_4$ requires C, 73.1; H, 5.3; N, 3.9)	
(3d)	46	*A*	176—177 [f]	Found: C, 70.3; H, 5.5; N, 3.7	1 718, 1 680
(5d)	3	*F*	173—175 [d]	Found: C, 70.7; H, 5.5; N, 5.55	1 720, 1 658
(6d)	27	*C* + *F*	140—141 [d]	Found: C, 70.7; H, 5.5; N, 3.45	1 725, 1 700
(7d)	12	*F*	130—131 [d]	Found: C, 70.6; H, 5.45; N, 3.5	1 738, 1 730, 1 700
(8d)			168—169 [d]	Found: C, 70.35; H, 5.45; N, 3.45	1 730, 1 710
				($C_{23}H_{21}NO_5$ requires C, 70.55; H, 5.4; N, 3.6)	

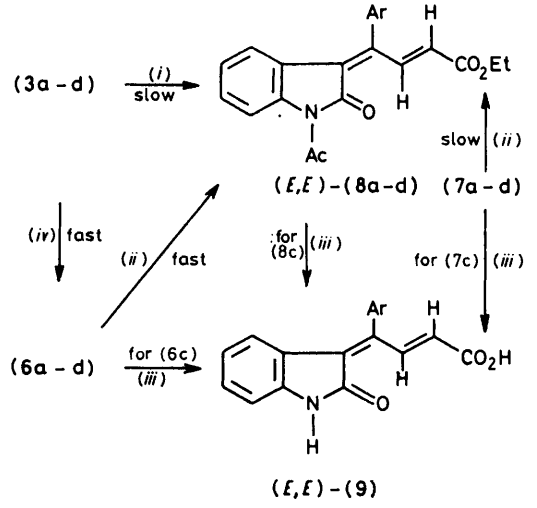
[a] *A*: Washing the reaction mixture with diethyl ether; *B*: column chromatography [Kieselgel H (Merck); cyclohexane–benzene–tetrahydrofuran (50 : 50 : 5)]; *C*: fractional crystallization from ethanol; *D*: column chromatography [Kieselgel; cyclohexane–ethyl acetate–methanol (90 : 10 : 2)]; *E*: column chromatography, [Kieselgel; cyclohexane–ethyl acetate (9 : 1)]; *F*: column chromatography [Kieselgel; cyclohexane–tetrahydrofuran (9 : 1)]. [b] The m.p.s of all compounds (6) and (7) are largely dependent on the rate of heating since isomerization to (8) occurs. [c] From ethyl acetate. [d] From ethanol. [e] From benzene. [f] From ethyl acetate–ethanol (1 : 1).

in aqueous acid media. Scheme 2 summarizes all the rearrangements and the reported experimental conditions give a reasonable order of the stability of the adducts.

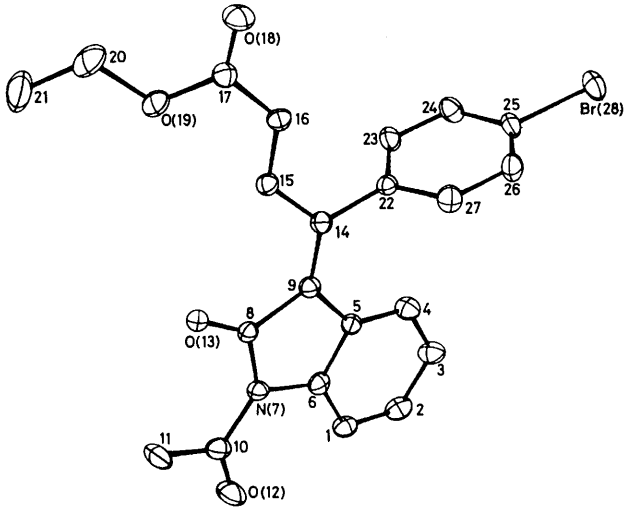
All these deductions were confirmed by an *X*-ray analysis of the bromo-derivative (8b), the ORTEP perspective view of which is shown in the Figure (see Experimental section for further details).

DISCUSSION

The formation of (3) and (5) can be rationalized in terms of (1,4) and (1,2) cycloadditions (Scheme 1), but these cannot explain the formation of (6) and (7). For these adducts the crystal structure determination of the isomer (8) was very useful and helped to show the stereochemical consequences of this reaction.



SCHEME 2 (*i*) CH_3CN, heat; (*ii*) benzene, heat; (*iii*) H^+, H_2O, heat; (*iv*) H^+, benzene, room temperature



ORTEP view of the molecular skeleton of (8b) (hydrogen atoms not included); the thermal ellipsoids are depicted according to the output of the last least-squares cycle

Indeed the (3*E*,2′*Z*)- and (3*Z*,2′*Z*)-configurations of (6) and (7) can only be explained by assuming a zwitterionic intermediate, which is formed by nucleophilic attack of the ethoxyethyne on the β position of the αβ-unsaturated carbonyl system (Scheme 3).

The more stable conformation (A) [9] can undergo either attack of the partially negative C-3 on the carbon

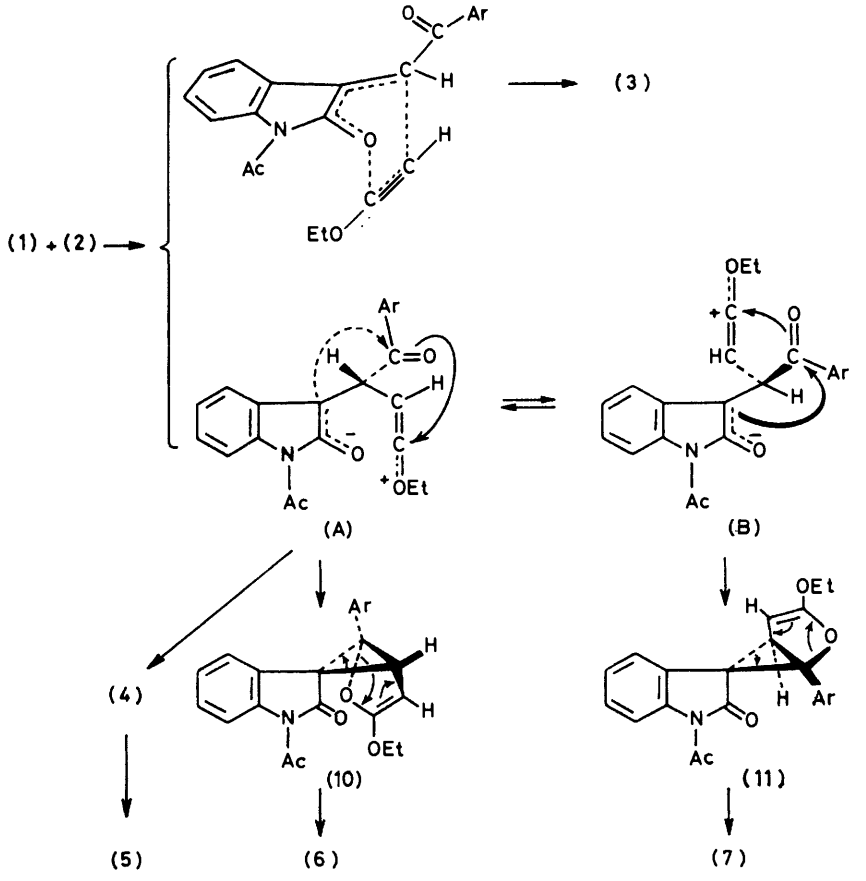
of the ketonic carbonyl, and ring closure of the oxygen to the partially positive carbon attached to the ethoxy-group leading to the spirobicyclic intermediate (10), or rotational isomerization to a different conformation, *i.e.* (B), which leads to the diastereoisomeric spirobicyclic intermediate (11).*

Both (10) and (11), upon electrocyclic ring opening, give open-chain unsaturated esters which have the olefinic hydrogens *cis* but, since the relative configuration of the Ar and lactam CO of (10) and (11) is retained in the open-chain adduct, (6) and (7) are formed respectively.

transition state and a zwitterion are simply two limiting structures of a hybrid in terms of hyperconjugation.[5]

This mechanism differs greatly from that proposed for the analogous pyran adduct obtained from the reaction of 4-arylidenepyrazol-5-ones and ynamines,[1] but resembles that proposed for the formation of dihydropyrans from the same 3-oxoindolylideneacetophenones and vinyl ether.[5]

This result is not unexpected if we remember that the energy of the LUMO of acetylenic ethers is lower than that of ynamines and also that the distortion of the co-



SCHEME 3

It seems reasonable to assume that the cyclobutene intermediate (4) can be formed from the same zwitterion, in the (A) conformation, if the nucleophilic attack occurs not on the carbonyl, but directly at the carbocationic end under the conditions discussed in the previous paper.[1] The alternative concerted process using all the triple bond π electrons (a [2 + 2 + 2] addition) seems less favourable.[10] In Scheme 3 the pyran adduct (3) is represented as originating from a concerted transition state, which can be considered either as a competing alternative pathway to the zwitterionic one, or as two parts of a comprehensive mechanism where a concerted

efficients follow the same trend. The resulting lower frontier-orbital energy separation between the highest occupied molecular orbital (HOMO) of the acetylene and the LUMO of the heterodiene, not balanced by the effect of a β electron-attracting substituent, ensures an increase in the ' concerted ' character of the cycloaddition.

The β-substituent effect can be clarified only if we compare the results reported in this paper with those (1,4-cycloadducts only) found if the same ethoxyethyne is allowed to react with 4-arylidenepyrazol-5-ones.[2,†]

* Of the six possible eclipsed and staggered rotameric conformations of the ' zwitterion,' three give (10) and three (11).

† 1,4-Cycloadducts only were also obtained from ethoxyethyne and 1-acetyl-3-(electron-attracting-substituted arylidene)-indolones.

EXPERIMENTAL

I.r. spectra were determined for Nujol mulls with a Perkin-Elmer 257 spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer R 12A spectrometer ($CDCl_3$ as solvent) by Dr. A. Gamba Invernizzi. Microanalyses were performed by Dr. L. Maggi Dacrema.

1-*Acetyl*-2-*oxo*-1H-*indolin*-3-*ylideneacetophenones* (1a—d). —(1c),[11] (1a),[11] and (1d) [11] were prepared by the reported methods. (1b) was obtained in 77% yield by acetylation [11] of the corresponding 1-unsubstituted derivative [12] as soft yellow needles, m.p. 173—174 °C (from ethyl acetate): $\nu_{max.}$ 1 745 (lactam CO), 1 703 (acetyl CO), 1 666 (ketone CO), and 1 628 (exocyclic double bond) cm^{-1}; δ 7.75 (s, vinylic H) (Found: C, 58.65; H, 3.3; N, 3.85; Br, 21.65. $C_{18}H_{12}BrNO_3$ requires C, 58.4; H, 3.3; N, 3.8; Br, 21.6%).

Reaction of the Oxoindolinylidene Derivatives (1a—d) *with Ethoxyethyne* (2).—To a suspension of (1) (5 mmol) in benzene (10 ml), was added ethoxyethyne [13] (3 ml), and the mixture stirred at room temperature until the starting product disappeared (t.l.c., kieselgel, benzene as eluant). The reaction time was in the range 4—14 days, the former for (1c) and the latter for (1a). The yellow suspension was filtered off and washed with diethyl ether, until pure (3) was obtained as a white solid. After setting aside and cooling of the concentrated mother liquors, several crops of yellow-orange crystalline solids were separated; t.l.c. (same eluants as for column chromatographic separations, see Table 3) showed some crops to be nearly pure adduct, others to be mixtures. Fractional crystallization from EtOH and/or column chromatography yielded pure (5), (6), and (7). From (1a), because of the long reaction time and facile isomerization, a considerable amount of (8a) was also obtained. The means of separation and the physical characters of all the adducts are reported in Table 3.

Acidic Rearrangement of (3) *into* (6).—A suspension of (3) (0.5 mmol) in dry benzene (10 ml) and a few crystals of toluene-*p*-sulphonic acid was stirred at room temperature for *ca.* 20 min. The yellow solution, after removal of solvent, gave compounds (6) in quantitative yield, identical in every respect with authentic samples.

Thermal Rearrangement of (3) *into* (8).—A suspension of 3 (0.2 mmol) in acetonitrile (5 ml) was heated in a sealed tube at 120 °C for *ca.* 10 days. The brown solution was evaporated to dryness and the oily residue was chromatographed [kieselgel; cyclohexane–ethyl acetate (8 : 2)]. Pure (8) (35—40%) was obtained as the first fraction (Table 3). A small amount of unreacted (3) could be separated as a second fraction.

Isomerization of (6) *into* (8).—A suspension of (6) (0.5 mmol) in dry benzene (20 ml) was refluxed for 4 h [2 h for (6a)]. The yellow solution, after evaporation to dryness, gave in nearly quantitative yield compounds (8), identical with the samples obtained by thermal rearrangement of (3).

Isomerization of (7) *into* (8).—A suspension of (7) (0.5 mmol) in dry benzene (20 ml) was refluxed for 12—13 days [3 days for (7a)]. The yellow solution, after evaporation to dryness, gave in nearly quantitative yield (8), identical with previously described samples.

(E,E)-3-(3-*Carboxy*-1-*phenylpropenylidene*)*indolin*-2-*one* (9).—A suspension of (6c) (0.25 mmol) in acetic acid (5 ml) and 4N HCl (0.8 ml) was refluxed for 2 h. The red solution was concentrated, and the crystalline residue was filtered off and washed with water; red prisms (80%), m.p. 263 °C decomp. (from acetic acid): $\nu_{max.}$ 3 260 (broad), 1 718, and 1 690 (broad) cm^{-1}; δ[$(CD_3)_2CO$] 9.62 (1 H, d, H-2′) and 5.62 [1 H, d, H-3′, J(2′,3′) 15.8 Hz] (Found: C, 74.05; H, 4.8; N, 4.9. $C_{18}H_{13}NO_3$ requires C, 74.2; H, 4.5; N, 4.8%). Comparable yields of (9) were obtained following this method, but starting from (7c) or (8c).

TABLE 4

Bond lengths (Å) and bond angles (°) (estimated standard deviations in parentheses) not involving hydrogen atoms (for atom numbering see Figure)

(*a*) Bond lengths

C(1)–C(2)	1.377(12)	C(14)–C(15)	1.472(10)
C(1)–C(6)	1.405(11)	C(14)–C(22)	1.500(10)
C(2)–C(3)	1.374(12)	C(15)–C(16)	1.305(10)
C(3)–C(4)	1.403(11)	C(16)–C(17)	1.477(11)
C(4)–C(5)	1.381(10)	C(17)–O(18)	1.213(9)
C(5)–C(6)	1.394(10)	C(17)–O(19)	1.335(9)
C(5)–C(9)	1.460(10)	O(19)–C(20)	1.488(10)
C(6)–N(7)	1.416(9)	C(20)–C(21)	1.469(14)
N(7)–C(8)	1.396(9)	C(22)–C(23)	1.385(10)
N(7)–C(10)	1.397(10)	C(22)–C(27)	1.355(10)
C(8)–C(9)	1.499(10)	C(23)–C(24)	1.384(11)
C(8)–O(13)	1.213(8)	C(24)–C(25)	1.330(11)
C(9)–C(14)	1.373(9)	C(25)–C(26)	1.401(11)
C(10)–C(11)	1.519(12)	C(26)–C(27)	1.385(11)
C(10)–O(12)	1.240(9)	C(25)–Br(28)	1.917(7)

(*b*) Bond angles

C(2)–C(1)–C(6)	117.7(8)	C(11)–C(10)–O(12)	122.3(8)
C(1)–C(2)–C(3)	121.9(7)	C(9)–C(14)–C(15)	123.5(7)
C(2)–C(3)–C(4)	120.5(8)	C(9)–C(14)–C(22)	119.5(6)
C(3)–C(4)–C(5)	118.6(7)	C(15)–C(14)–C(22)	117.0(6)
C(4)–C(5)–C(6)	120.3(7)	C(14)–C(15)–C(16)	122.9(7)
C(4)–C(5)–C(9)	132.3(7)	C(15)–C(16)–C(17)	124.3(7)
C(6)–C(5)–C(9)	107.3(6)	C(16)–C(17)–O(18)	123.5(8)
C(1)–C(6)–C(5)	120.9(8)	C(14)–C(22)–C(27)	120.8(7)
C(1)–C(6)–N(7)	128.4(7)	C(16)–C(17)–O(19)	112.7(7)
C(5)–C(6)–N(7)	110.6(6)	O(18)–C(17)–C(19)	123.8(8)
C(6)–N(7)–C(8)	109.0(6)	C(17)–O(19)–C(20)	116.8(7)
C(6)–N(7)–C(10)	126.3(6)	O(19)–C(20)–C(21)	107.6(8)
C(8)–N(7)–C(10)	124.2(7)	C(14)–C(22)–C(23)	119.9(7)
N(7)–C(8)–C(9)	107.0(6)	C(23)–C(22)–C(27)	119.3(7)
N(7)–C(8)–O(13)	124.7(7)	C(22)–C(23)–C(24)	120.2(7)
C(9)–C(8)–O(13)	128.3(7)	C(23)–C(24)–C(25)	119.6(7)
C(5)–C(9)–C(8)	106.0(6)	C(24)–C(25)–C(26)	121.9(7)
C(5)–C(9)–C(14)	129.9(7)	C(24)–C(25)–Br(28)	121.2(6)
C(8)–C(9)–C(14)	124.0(7)	C(26)–C(25)–Br(28)	116.8(7)
N(7)–C(10)–C(11)	120.7(7)	C(25)–C(26)–C(27)	117.4(7)
N(7)–C(10)–O(12)	117.0(8)	C(22)–C(27)–C(26)	121.4(7)

TABLE 5

Relevant torsion angles (°), with estimated standard deviations in parentheses

C(14)–C(9)–C(8)–O(13)	−178.7(11)
C(9)–C(8)–N(7)–C(10)	−9.1(5)
O(13)–C(8)–N(7)–C(10)	172.1(7)
C(10)–N(7)–C(6)–C(5)	9.5(6)
C(10)–N(7)–C(6)–C(1)	−169.6(10)
C(11)–C(10)–N(7)–C(8)	175.4(7)
C(11)–C(10)–N(7)–C(6)	−13.1(7)
O(12)–C(10)–N(7)–C(8)	−3.2(5)
O(12)–C(10)–N(7)–C(6)	168.3(7)
C(8)–C(9)–C(14)–C(15)	172.5(7)
C(8)–C(9)–C(14)–C(22)	−6.1(5)
C(5)–C(9)–C(14)–C(15)	−5.5(5)
C(5)–C(9)–C(14)–C(22)	175.8(7)
C(9)–C(14)–C(22)–C(23)	96.6(9)
C(9)–C(14)–C(22)–C(27)	−84.2(6)
C(15)–C(14)–C(22)–C(23)	−82.2(8)
C(15)–C(14)–C(22)–C(27)	97.0(6)
C(9)–C(14)–C(15)–C(16)	−3.9(5)
C(14)–C(15)–C(16)–C(17)	0.5(5)
C(15)–C(16)–C(17)–O(18)	−13.1(6)
C(15)–C(16)–C(17)–O(19)	168.1(10)
C(16)–C(17)–O(19)–C(20)	0.9(8)
O(18)–C(17)–O(19)–C(20)	−177.8(8)
C(17)–O(19)–C(20)–C(21)	−12.5(9)

TABLE 6

Distances (Å) of atoms from their least-squares planes; each plane comprises the atoms whose distances from it are listed (estimated standard deviations <0.01 Å)

Indolinone ring	C(1) −0.001	C(2) 0.028	C(3) 0.037	C(4) 0.007	C(5) −0.026	C(6) −0.024	N(7) −0.029	C(8) 0.012	C(9) −0.001	O(13) 0.030	C(14) −0.019
Diene–ester system	C(14) 0.004	C(15) 0.075	C(16) −0.101	C(17) −0.026	O(18) 0.038	O(19) −0.010	C(20) 0.041				
Br-phenyl ring	C(14) −0.088	C(22) 0.011	C(23) 0.041	C(24) 0.054	C(25) 0.034	C(26) 0.037	C(27) 0.054	Br(28) −0.002			

X-*Ray Analysis.*—*Crystal data.* (8b): $C_{22}H_{18}BrNO_4$, yellow-orange needles, space group $P2_1/n$, $Z = 4$, $a = 11.215(4)$, $b = 20.651(6)$, $c = 8.877(3)$ Å, $\beta = 100.6(5)°$. The crystal used had dimensions 0.13 × 0.13 × 0.48 mm. Intensity data were collected on a Philips PW 1100 computer-controlled four-circle diffractometer using the ω—2θ scan technique, graphite-monochromatized Cu-K_α radiation, $\lambda = 1.5418$ Å. 2 075 Independent reflections were collected up to $\theta_{max.}$ 50° and processed according to the method of Davies and Gatehouse [14] so as to yield values of F_o and $\sigma(F_o)$; the 1 617 reflections with $I > 3\sigma(I)$ were regarded as observed. The structure was solved by use of heavy-atom methods (Patterson and F_o syntheses) and anisotropically refined with the program ORFLS;[15] co-ordinates for hydrogen atoms (except for those belonging to the two methyl groups) were determined on the basis of geometrical considerations and checked on a difference-Fourier map. They were inserted but not allowed to vary during the refinement procedures. The final R was 0.052 for the observed reflections. Scattering factors for neutral atoms were those listed by Doyle and Turner [16] and for the hydrogen atoms were those of Stewart *et al.*[17] Bond lengths and angles not involving hydrogen atoms are listed in Table 4, the more significant torsion angles are given in Table 5, and an analysis of the planarity of the rings and of the conjugated systems is provided in Table 6. Tables of structure factors, atomic fractional co-ordinates, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22367 (17 pp.).*

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