Activating Groups for the Ring Expansion of Coumarin by Diazoethane: Benzoyl, Pivaloyl, Arylsulphonyl, Arylsulphinyl, and Nitro

By **Francis M. Dean** * and **B. Kevin Park**, The Robert Robinson Laboratories, The University of Liverpool, Liverpool L69 3BX

The slow reaction between 3-ethoxycarbonylcoumarin and diazoethane affords the 4-ethyl derivative as the main product. 3-Benzoylcoumarin reacts faster but the main product is still the 4-ethyl derivative, though some ring expansion occurs, giving the oxepin derivative (VIII). 3-Pivaloylcoumarin suffers more ring expansion and gives an oxepin derivative (VIb) of a kind previously postulated in this work but never isolated. This oxepin further adds diazoethane giving a pyrazoline (IXa), comparable to (IXb) which is the first isolable product from 3-acetylcoumarin. Thermolysis of (IXa) gives largely the ethyloxepin (X), and the desired oxocin derivative (XIa) is formed to a minor extent only.

The unstable primary adduct from diazoethane and 3-(4-methylphenylsulphonyl)coumarin can be isolated but again collapses giving mainly the 4-ethyl derivative with a little of the oxepin derivative (XVI); no inverse addition was noted. The adduct from the corresponding sulphinylcoumarin eliminated the sulphenic acid immediately thus affording a simple synthesis of the [1]benzopyrano[3,4-*c*]pyrazole (XIXa) and its relatives. The use of 2-diazopropane gave the corresponding 3*H*-pyrazole derivative (XX) and of sodium azide the 1,2,3-triazole (XXII).

The reaction between 3-nitrocoumarin and diazoethane gave the 4-ethyl-3-nitrocoumarin in lesser amounts and considerable ring expansion resulted in the pyrazoline (XXIV), but small amounts of the cyclopropane derivatives (XXV) and (XXVI) were also noted as well as a trace of the cyclic nitrone (XXVII). The cyclopropane (XXVI) is the main product from thermolysis of the pyrazoline (XXIV), and no homologation was detected. The pyrazoline is itself further attacked by diazoethane (but not by diazomethane or 2-diazopropane) and suffers conversion of its lactonic carbonyl group into an oxiran system as in (XXX).

It is concluded that, in general, acetyl is the best activating group for inducing a series of ring homologations.

DIAZOETHANE partly alkylates 3-acetylcoumarin (Ia) giving the 4-ethyl derivative (Ib) and partly induces a ring expansion [1a] that has been developed into a synthetically useful tool.[2a] Further studies have been made in order to determine whether acetyl is the best activating group for the purpose; in a parallel study it has been shown that the cyano-group induces alkylation specifically and is therefore useless for ring expansion purposes.[3] Here we report that ethoxycarbonyl hardly provides enough activation of any kind; that although benzoyl, pivaloyl, and arylsulphonyl groups are less effective in producing successive ring expansions than is acetyl, they sometimes allow the isolation of intermediates of kinds that had previously escaped detection; that arylsulphinylcoumarin adds diazoethane but the adduct preferentially eliminates the activating group, thus providing a simple synthesis of derivatives of [1]benzopyrano[3,4-*c*]pyrazole; [2c] and that while the nitro-group favours ring expansion, it also induces the formation of small rings, the most remarkable being the formation of an oxiran derivative from an ester carbonyl group.[2b] In ring expansion studies, therefore, acetyl is the best activating group.

3-Ethoxycarbonylcoumarin [4] added diazoethane too slowly for the present purposes, and the adduct (IIa) could not be isolated as it collapsed readily giving the alkylated coumarin (IIIa) as the only isolable product. This compound has been described previously,[5] and the

[1] R. Clinging, F. M. Dean, and L. E. Houghton, (*a*) *J.C.S. Perkin I*, 1974, 66; (*b*) *J. Chem. Soc.* (*C*), 1970, 897.

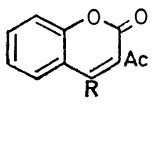
[2] F. M. Dean and B. K. Park, (*a*) *J.C.S. Chem. Comm.*, 1975, 142; (*b*) *ibid.*, 1974, 162; (*c*) *Tetrahedron Letters*, 1974, 4275.

[3] R. Clinging, F. M. Dean, L. E. Houghton, and B. K. Park, *Tetrahedron Letters*, in the press.

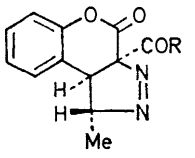
[4] E. C. Horning, M. G. Horning, and D. A. Dimming, *Org. Synth.*, 1955, Coll. Vol. III, p. 715.

[5] C. Wiener, C. H. Schroeder, and K. P. Link, *J. Amer. Chem. Soc.*, 1957, **79**, 5301.

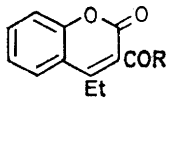
n.m.r. spectrum (Table) confirmed the presence of the two ethyl groups. 3-Benzoylcoumarin [6] reacted much more quickly and the alkylated coumarin (IIIb) was obtained in relative high yield. This was disappointing, as earlier discussions [1,3,7-9] had led us to believe that with the system in conformation (IVa), elimination of coumarin (IIIb) but the u.v. spectrum is not that of a coumarin though both lactone and ketone carbonyl bands appear in the i.r. spectrum. The compound gives a coloured complex with iron(III) salts and the n.m.r. spectrum (Table) is compatible only with the proton arrangement shown.



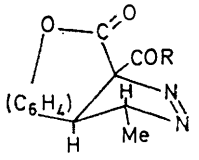
(I) a; R = H
b; R = Et



(II) a; R = OEt
b; R = Ph



(III) a; R = OEt
b; R = Ph
c; R = CMe_3



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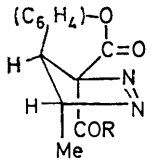

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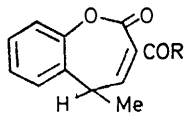

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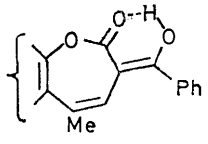
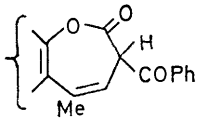
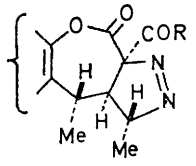


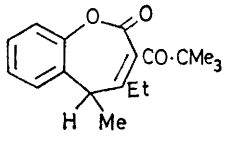
(VII)



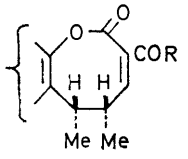
(VIII)



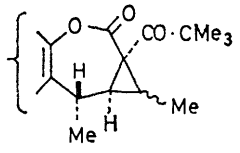
(IX) a; R = CMe_3
b; R = Me



(X)



(XI) a; R = CMe_3
b; R = Me



(XII)

nitrogen would be concerted with hydrogen migration (= alkylation) but that the 1,3-di(pseudo)axial interaction between the methyl and bulky benzoyl groups would strongly promote conformational inversion to (Va) in which elimination would be concerted with aryl migration (= ring expansion). Some ring expansion does occur, however, and presumably it gives the conjugated enedione (VIa) in the first place, but prototropy at once leads to the completely conjugated enol (VII) and thence to the 3*H*-benzoxepinone (VIII) actually isolated. This is isomeric with the 4-ethyl-

In 3-pivaloylcoumarin the activating group is a particularly bulky one, likely to be able to maintain a pyrazoline conformation much closer to (IVb) than to (Vb). Accordingly, the compound added diazoethane and the very unstable pyrazoline (not isolated) underwent extensive ring expansion, and not much of the 4-ethylcoumarin (IIIc) was formed. In this case the ring expansion supplied the conjugated enone (VIb) and therefore provided the first direct evidence for the participation of such species in the more complex sequences normally observed. It seems that prototropy could be

[6] N. P. Buu-Hoï, G. Daint-Ruf, T. B. Loc, and N. G. Xuong, *J. Chem. Soc.*, 1957, 2593.

[7] D. E. McGreer and J. W. McKinley, *Canad. J. Chem.*, 1971, **49**, 105; D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. Wong, *ibid.*, 1965, **34**, 1407.

[8] J. Hamelin and R. Carrié, *Bull. Soc. chim. France*, 1968, 3000; 1972, 2054; R. Danion-Bougot and R. Carrié, *ibid.*, 1968, 2526.

[9] J. P. Deleux, G. Leroy, and J. Weiler, *Tetrahedron*, 1973, **29**, 1135.

avoided because the compounds crystallised readily and chromatography was unnecessary. Moreover, the bulk of the trimethylmethyl group may cause the pivaloyl group to rotate out of conjugation with the alkene double bond and thus reduce the ease of prototropy; the i.r. carbonyl bands at 1 715 and 1 692 cm^{-1} suggest that the lactonic carbonyl group is conjugated fully but the ketonic group incompletely. The n.m.r. spectrum (Table) establishes the proton sequence in the oxepin ring and suggests a torsion angle of *ca.* 135° between the vinylic proton and its neighbour. This angle suggests that the oxepin ring is somewhat saucer-shaped, with the methyl group disposed pseudoequatorially, and thus explains the low field at which this group resonates.

Nevertheless, the oxepin (VIb) was unstable on silica columns, *etc.*, so the yield could not be determined directly. Consequently, the crude reaction mixture producing it was treated with more diazoethane and the oxepin isolated as the relatively stable insoluble adduct (IXa). From 3-acetylcoumarin and diazoethane, the corresponding adduct (IXb) is formed directly, none of the intervening compounds being isolable. The structure of the new adduct follows from its spectroscopic properties, especially its n.m.r. spectrum (Table), which is closely similar to that of the acetyl analogue.[1a] The new pyrazoline was isolated in 44% yield, and the ethylcoumarin (IIIc) in 34% yield; for the first time in studies on coumarin homologation, therefore, ring expansion had become more important than plain alkylation.

The resemblance between the n.m.r. spectra of the two adducts (IXa and b) extends to the coupling constants, suggesting that the pivaloyl group does not unduly disturb the conformation of the system and that the pyrazoline segment would probably be held approximately in a conformation like that in (IV), *i.e.* the conformation best suited to further ring expansion. In practice the

^{1}H N.m.r. spectra [a] (solvent deuteriochloroform; τ scale; at 100 MHz)

Coumarins

Compound	O·CH_2Me	C·CH_2Me	O·CH$_2$·CH_3	C·CH$_2$·CH_3	ArCH$_3$	CMe$_3$	H-4
(IIIc; H for Et)						8.67	1.37
(XIIIb)					7.68		1.56
(IIIa)	5.52 (q, 7)	7.12 (q, 7)	8.51 (t, 7)	8.57 (t, 7)			
(IIIb)		7.29 (q, 7.5)		8.74 (t, 7.5)			
(IIIc)		7.34 (q, 7)		8.70 (t, 7) [b]		8.70 [b]	
(XV)		6.34 (q, 7)		8.50 (t, 7)	7.60		
(XXXIIIb)		7.17 (q, 7)		8.60 (t, 7)			

Benzoxepin derivatives

	H-3	H-4	H-5	Me(C-5)	ArCH$_3$	CMe$_3$	CH_3·CH$_2$	CH$_3$·CH_2
(VIII)	5.62 (dq; 5.5, 1.5)	3.50 (dq; 5.5, 1.5)		7.74 (dd; 1.5, 1.5)				
(XVI)	5.84 (dq; 6, 1.5)	4.02 (dq; 6, 1.5)		7.78 (dd; 1.5, 1.5)	7.58			
(VIb)		3.22 (d; 7)	6.16 (dq; 7, 6.5)	8.43 (d; 7)		8.90		
(X)			6.59 (q; 7)	8.50 (d; 7)		8.90	8.83 (t; 7.5)	7.82 (q; 7.5)

Pyrazoline derivatives

	H-3	H-3a	H-4	Me(C-3)	Me(C-4)	CMe$_3$	H-3′	Me(C-3′)
(IXa)	5.76 (dq; 8. 7)	7.38 (dd; 8, 12)	7.00 (dq; 12, 6.5)	8.34 (d; 7)	8.55 (d; 6.5)	8.70		
(XXIV)	5.17 (dq; 9, 7)	7.21 (dd; 12, 9)	6.75 (dq; 12, 7)	8.27 (d; 7)	8.48 (d; 7)			
(XXX) [c]	5.50 (dq; 9, 7)	7.36 (dd; 6, 9)	6.63 (dq; 6,7)	8.38 (d; 7)	8.40 (d; 7)		6.38 (q; 4.5)	8.54 (d; 4.5)

Cyclopropane derivatives

	H-1	H-8	H-8a	Me(C-1)	Me(C-8)	CMe$_3$
(XII) [b]	7.9 (m; ?)	7.30 (dq; 11, 7)	7.9 (m; ?)	9.00 (d; 6)	8.53 (d; 7)	8.80
(XXVI) [b]	*ca.* 7.7 (dq; ?)	7.21 (dq; 10, 6.75)	*ca.* 7.7 (m; ?)	8.56 (d; 6.5)	8.47 (d; 6.75)	
(XXV)	6.9 (dq; 10, 7)		6.53 (H-7b) (d; 10)	8.95 (d; 7)		

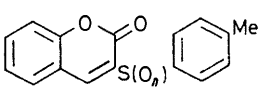
Other

	H-1	H-9b	Me
(XXVII)	4.82 (dq; 11, 6)	5.23 (d; 11)	8.05 (d; 6)

[a] Excluding aromatic resonances. All intensities were as required by the assignments. Multiplicities and coupling constants (Hz) are given in parentheses below the chemical shifts to which they refer. [b] Analysis confused by overlapping bands. [c] Decoupling experiments confirmed the interaction of H-3a with H-3 and with H-4 and also the identification of the methyl groups.

pivaloylpyrazoline was rather stable to thermolysis in benzene, and alkylation again became more important (70%) than the intended ring expansion (20%). Models failed to disclose any clear, single reason for this reversal in passing from the pyranopyrazole (IVb) to the oxepinopyrazole (IXa), but we think it may be connected with the difficulty of getting both the lactonic and the ketonic carbonyl groups into conjugation with the incipient alkene double bond as (IXa) collapses. The pivaloyl group is hampered by its size, while the lactonic group is severely contorted by ring constraints. Thus conjugation is more easily achieved for hydrogen migration, and the argument would therefore explain both the unusual stability of the adduct and the reversal in its mode of collapse. The importance of such conjugation effects has been stressed elsewhere.[1b,3] In the ethylated oxepin (X) only one carbonyl i.r. band is seen (at 1 710 cm^{-1}) indicating that, as in similar examples, the ketonic group has to rotate out of conjugation so that the frequency rises and overlaps that of the lactone carbonyl group; the n.m.r. spectrum (Table) shows that both an ethyl group and an ethylidene group are present and leaves no doubt as to the structure. The spectroscopic characteristics of the oxocin derivative (XIa) are nearly identical with those of the corresponding acetyl compound [1a] (XIb). The same thermolysis produces a small amount of the cyclopropane derivative (XII), the structure of which was deduced mainly from the n.m.r. spectrum (Table), and though this has not yet been fully analysed it is clear that the torsion angle between the benzylic and adjacent cyclopropane protons must approach 180° so that the partial stereochemistry is as shown.

3-(4-Methylphenylsulphonyl)coumarin (XIIIa) was readily prepared from methyl 4-methylphenylsulphonylacetate and 2-hydroxybenzaldehyde. With diazoethane it gave the adduct (XIV) as an unstable, crystalline solid. Initial adducts of this type have normally evaded isolation in our work and the fact that this one could be isolated is probably more a result of its high crystallinity and relative insolubility than of any special stability. In the absence of an aromatic substituent, unsaturated sulphones may add diazomethane giving adducts stable enough to be recrystallised,[10] but our compound was too unstable even for a satisfactory n.m.r. spectrum to be



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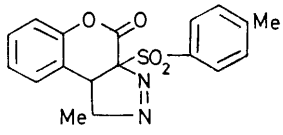
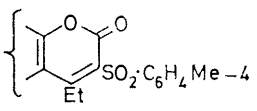
b ; n = 1



(XIV)



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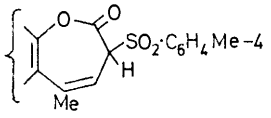
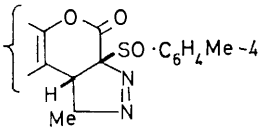
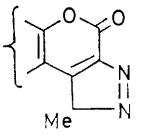


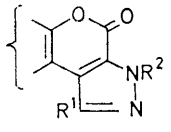
(XVI)



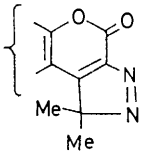
(XVII)



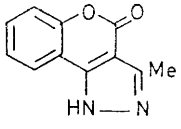
(XVIII)



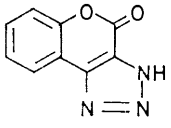
(XIX) a ; R^1 = Me, R^2 = H
b ; R^1 = Me, R^2 = Et
c ; R^1 = H, R^2 = Me



(XX)



(XXI)



(XXII)

[10] R. Helder, T. Doornbos, J. Strating, and B. Zwanenburg, *Tetrahedron*, 1973, **29**, 1375; J. S. Meek and J. S. Fowler, *J. Org. Chem.*, 1968, **33**, 985.

obtained. It collapsed at once in refluxing benzene giving the 4-ethylcoumarin (XV) as the major product along with some of the benzoxepin (XVI). Evidently there has been a prototropic shift as there was in the 3-benzoylcoumarin series, but we found no sign of any inverse addition comparable to that reported for styryl sulphones [11] nor did we observe an elimination of arenesulphonic acid such as is sometimes noted.[10]

Prepared from methyl 4-methylsulphinylacetate and 2-hydroxybenzaldehyde, 3-(4-methylphenylsulphinyl)-coumarin (XIIIb) was presumably converted into the adduct (XVII), which must have immediately eliminated the arenesulphenic acid leaving the 3*H*-pyrazole derivative (XVIII), though the compounds isolated were the tautomer (XIXa) and its ethylation product (XIXb). Diazoalkanes are known to be basic enough to catalyse tautomerisation [12] and other reactions.[13] The result is novel in these studies, and provides a useful synthesis of pyrano[3,4-*c*]pyrazole compounds since the yields are nearly quantitative. No doubt the sequence is aided by the fact that, because the 1,3-dipolar addition of diazoethane is *cis*, the geometry of the adduct (XVII) is precisely suited to the *cis*-elimination of the sulphonic acid on the opposite side of the molecule. Most sulphenic acid eliminations occur readily only at higher temperatures [14] and it may be that the resonance energy gained, by restoring complete conjugation in the coumarin ring promotes this one in the cold. Diazomethane behaves as does diazoethane giving (XIXc), while 2-diazopropane affords the 3*H*-pyrazole derivative (XX) since tautomerisation is impossible. Before this work, the reaction between an allylic sulphoxide and diazomethane was the only one recorded between an unsaturated sulphoxide and a diazoalkane.[15] The reaction was an unusual one likely to be peculiar to that type of substrate; and since, as noted above, some sulphones may undergo inverse addition with diazoalkanes, the possibility in the present case of inverse addition could not be left unchecked. However, the inverse addition of diazoethane to the sulphoxide would have given a benzopyranopyrazole (XXI) that had already been described; [16] a sample was prepared and found to differ from the diazoethane product.

Little success attended efforts to extend the addition–elimination reaction of the sulphinylcoumarin to 1,3-dipoles other than diazoalkanes. Certainly, with sodium azide in dimethylformamide at 90 °C, a high yield of the pyranotriazole (XXII) resulted, but there was no reaction between the coumarin and benzonitrile oxide, 4-methylbenzonitrile oxide, phenyl azide, or trimethylsilyl azide. So complete a failure was unexpected, since there is ample reason to suppose that azides and nitrile oxides would resemble diazoalkanes closely in addition reactions.[17,18]

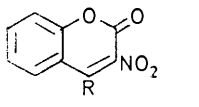
Finally, we examined nitro as the activating group. The reaction between 3-nitrocoumarin (XXIIIa) and diazoethane was more complex than any of the other reactions studied. The simple alkylation, giving the 4-ethylcoumarin (XXIIIb), was less important than usual, and the main result was ring expansion and subsequent addition giving the oxepinopyrazole (XXIV). This compound was not easily studied as it was neither very stable nor very soluble in the common solvents. Nevertheless, the n.m.r. spectrum (Table) is so similar to that of the acetyl analogue [1a] (IXb) that the proton sequences and relative configurations must be identical and the conformations nearly so. Two minor products were found to be cyclopropane derivatives. One has to be assigned structure (XXV) because of its n.m.r. spectrum (Table) and i.r. evidence for the presence of nitro and lactone carbonyl groups; no doubt the compound is formed by loss of nitrogen from the initial diazoethane–coumarin adduct but this is the only example where a cyclopropane ring is formed at this stage. The torsional coupling constant (10 Hz) for the methine protons appears to establish the *cis*-configuration.[19] The other cyclopropane derivative is allocated structure (XXVI), mainly on the basis of the n.m.r. spectrum (Table) from which the only stereochemical deduction that could be made with certainty was that the benzylic and adjacent methine protons have the *trans* dipseudoaxial relation (J 10 Hz). Evidently the compound is formed as was the congener, but from the pyrazoline (XXIV), and this reaction was the main one when the pyrazoline itself was warmed in benzene, no ring expansion whatever being detected.

The diazoethane reaction also supplied traces of the isoxazoline (XXVII). The n.m.r. spectrum (Table) established the presence of the ethylidene group and the *cis* relation of the methine protons followed from an analysis [20] of the similar compound (XXVIII). The i.r. spectrum showed that the lactonic grouping was intact, but possessed no bands appropriate to a nitro-group; instead of these, strong bands appeared at 1 625 and 1 145 cm^{-1} as in nitrones.[21,22] The mass spectrum confirmed the nitrone formulation, particularly by demonstrating the loss from the molecular ion of one oxygen

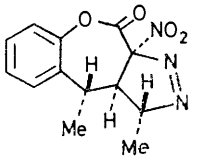
[11] W. E. Parham, F. D. Blake, and D. R. Theissen, *J. Org. Chem.*, 1962, **27**, 2415.
[12] R. Clinging and F. M. Dean, *J. Chem. Soc.* (*C*), 1971, 3668.
[13] H. Bredereck, R. Sieber, and L. Kamphenkel, *Chem. Ber.*, 1956, **89**, 1169.
[14] I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.* (*C*), 1967, 302; B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, 1973, **95**, 6840; M. von Strandtman, S. Klutchko, M. P. Cohen, and J. Shand, *J. Heterocyclic Chem.*, 1972, **9**, 171.
[15] L. Veniard and G. Pourcelot, *Bull. Soc. chim. France*, 1973, 2746.
[16] A. Mustafa, O. H. Hishmat, A. A. Nawar, and K. M. A. Khalil, *Annalen*, 1965, **684**, 194.
[17] K. N. Houk, J. Sims, R. E. Duke, R. W. Strozier, and J. K. George, *J. Amer. Chem. Soc.*, 1973, **95**, 7287.
[18] R. Huisgen and K. Bast, *Chem. Ber.*, 1973, **106**, 3312.
[19] L. M. Jackman and S. Sternhell, 'Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 286.
[20] M. Christl, R. Huisgen, and R. Sustmann, *Chem. Ber.*, 1973, **106**, 3275.
[21] H. Schechter and F. Conrad, *J. Amer. Chem. Soc.*, 1954, **76**, 2716.
[22] G. R. Delpierre and M. Lamchen, *Quart. Rev.*, 1965, **19**, 329.

atom, a highly characteristic feature.[23] The reaction of 1,3,5-trinitrobenzene with diazomethane has previously been reported [24] to give the similar cyclic nitrone (XXIX).

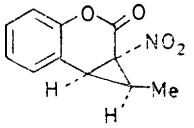
Most remarkably, the reaction between diazoethane and 3-nitrocoumarin did not stop at the oxepinopyrazole (XXIV) but continued until this compound had been converted into the oxiran (XXX). Ketonic carbonyl groups are well known to yield oxirans with diazoalkanes



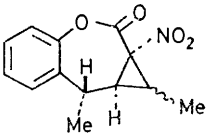
(XXIII) a; R = H
b; R = Et



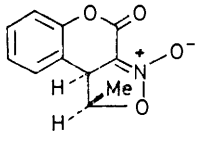
(XXIV)



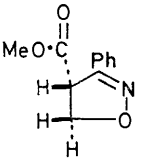
(XXV)



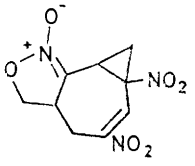
(XXVI)



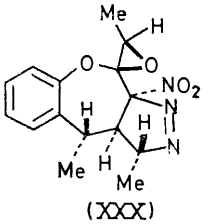
(XXVII)



(XXVIII)



(XXIX)



(XXX)

especially when electron-withdrawing substituents are present,[25] and we described an example earlier in this series.[1b] To our knowledge, however, ester carbonyl groups have not before been observed in oxiran formation.[2b] Any attack on an ester group is unusual, although the idea has been employed [26] to explain an intramolecular rearrangement in which, however, the ester group was regenerated.

The n.m.r. spectrum (Table) shows that the spin system of the original pyrazoline has been retained, and a new, independent ethylidene group introduced. The i.r. bands characteristic of the nitro-group are unaffected, and no OH or NH bands are seen; on the other hand, the lactonic carbonyl band is absent. The formation of an oxiran derivative from the lactone group seems the sole possibility, notwithstanding its unexpectedness. The view is strengthened by the relative stability of the compound, one activating group having been removed. It is also strongly supported by the chemical shift of the new ethylidene methine proton and by the small value of its torsional coupling constant, both being characteristic of oxiran systems.[27,28] The torsional coupling of the two oxiran methine protons is much less than it is in the parent pyrazoline (XXIV), but a change in this relatively flexible part of the molecule would follow the change in hybridisation at the carbonyl carbon atom, and a rotation from a torsion angle near 180° to one near 35° is seen from models to be acceptable. The relative stereochemistry has been assigned to the oxiran system mainly to place the methyl group as far as possible from other groups and is tentative.

The carbonyl group may be susceptible to diazoalkane attack because of the accumulation of strongly electron-attracting groups adjacent to it. Both the nitro- and the azo-group appear to be essential, for we have examined a number of other lactones bearing either group, but not both, without finding any evidence for reaction. It is also remarkable that neither diazomethane nor 2-diazopropane could be induced to react with (XXIV). It may be that diazomethane is not nucleophilic enough, so that its reaction to form an oxiran is slower than the general decomposition of the unstable substrate; and that while 2-diazopropane is sufficiently nucleophilic, its bulk prevents it from reaching the reaction centre.

EXPERIMENTAL

Diazoethane in ether was repeatedly dried over pellets of potassium hydroxide and slowly distilled immediately before use. Non-hydroxylic solvents were dried over calcium hydride and redistilled. The light petroleum used was the fraction of b.p. 60—80°. I.r. spectra (diagnostic bands only) are quoted for KBr discs if no other phase is specified. U.v. spectra were determined for solutions (*ca.* 10^{-3}M) in ethanol.

3-Ethoxycarbonyl-4-ethylcoumarin-3-carboxylate.— Diazoethane (*ca.* 1 g) in ether (50 ml) was added to 3-ethoxycarbonylcoumarin [4] (1.0 g) in tetrahydrofuran (50 ml) and the mixture was stored in the dark at 0 °C for 18 h. Removal of volatile materials *in vacuo* at 0 °C left an unstable oil that would not crystallise and was kept in ether (10 ml) at 23 °C until nitrogen was no longer evolved (*ca.* 5 h). The oily product was purified by preparative t.l.c. on silica with ether–light petroleum (2 : 1 v/v) for development. Isolation of the main band with chloroform and filtration through Celite gave the 4-ethyl derivative (IIIa) (0.45 g),

[23] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectra of Organic Compounds,' Holden–Day, San Francisco, 1974, p. 329.
[24] J. C. van Velzen, C. Kruk, and T. J. DeBoer, *Rec. Trav. chim.*, 1971, **90**, 842.
[25] B. Eistert, in 'Newer Methods of Preparative Organic Chemistry,' Interscience, New York, 1948, p. 513.
[26] E. H. Billett and I. Fleming, *J.C.S. Perkin I*, 1973, 1658; I. Fleming and S. W. Hanson, *ibid.*, p. 1669.
[27] E. L. Musher and R. G. Gordon, *J. Chem. Phys.*, 1962, **36**, 3097.
[28] S. J. Bois, *J. Org. Chem.*, 1962, **27**, 3532.

m.p. 50—51° (from ether–hexane) (lit.,[5] 50—52°), $\nu_{max.}$ (KBr) 1 720br (lactone and ester) and 1 600 cm^{-1} (aromatic).

3-*Benzoylcoumarin and Diazoethane*.—3-Benzoylcoumarin [6] (5.0 g) in ether (200 ml) and tetrahydrofuran (20 ml) was treated at 0 °C with diazoethane (*ca.* 5.0 g) in ether during 30 min. Volatilisation of solvents and excess of reagent at 0 °C *in vacuo* gave a yellow oil that rapidly lost nitrogen at room temperature and then when kept in contact with ether deposited a solid which was purified from benzene–light petroleum giving 3-*benzoyl*-4-*ethylcoumarin* (IIIb) as large needles (3.1 g), m.p. 115—116°, $\lambda_{max.}$ 254, 280, and 312 nm (log ε 3.93, 3.95, and 3.73), $\nu_{max.}$ (KBr) 1 700 (lactone) and 1 680 cm^{-1} (benzoyl) (Found: C, 77.5; H, 5.1%; *M*, 278. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%; *M*, 278).

After removal of the benzoylethylcoumarin, the ether solution was concentrated to an oil (2.1 g) which was chromatographed on silica (84 g), initially from benzene–light petroleum (4 : 1 v/v). The main band gave another oil which was treated in ether with decolourising charcoal and then gradually crystallised giving 3-*benzoyl*-5-*methyl*-1-*benzoxepin*-2(3H)-*one* (VIII) as prisms (0.35 g), m.p. 116—117°, $\lambda_{max.}$ 247 nm (log ε 4.34), $\nu_{max.}$ 1 753 (lactone) and 1 690 cm^{-1} (benzoyl) (Found: C, 77.7; H, 5.0%; *M*, 278. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%; *M*, 278). This compound imparted a green colour to ethanolic iron(III) chloride. The chromatography was continued with benzene–chloroform (7 : 3 v/v) as eluant and supplied more 3-benzoyl-4-ethylcoumarin (0.68 g; total yield 72%).

3-*Pivaloylcoumarin*.—A mixture of 2-hydroxybenzaldehyde (0.61 g) methyl 4,4,4-trimethyl-3-oxobutanoate [29] (0.86 g) and piperidine (3 drops) was heated on a steam-bath for 30 min, and the deep orange product was chromatographed on silica (90 g) from benzene. The main fraction crystallised from ether–hexane giving 3-*pivaloylcoumarin* as plates (0.86 g), m.p. 89—90°, $\nu_{max.}$ 1 715 (lactone) and 1 690 cm^{-1} (pivaloyl) (Found: C, 73.1; H, 6.3%; *M*, 230. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.1%; *M*, 230).

3-*Pivaloylcoumarin and Diazoethane*.—A mixture of 3-pivaloylcoumarin (1.0 g) in ether (100 ml) and diazoethane (*ca.* 1 g) also in ether (100 ml) kept at 0 °C for 30 min gave an unstable product isolated by removal *in vacuo* of volatile materials, and then left in fresh ether (20 ml) until effervescence ceased (*ca.* 3 h). The resulting oil crystallised in contact with hexane in ice giving 5-*methyl*-3-*pivaloyl*-1-*benzoxepin*-2(5H)-*one* (VIb) as prisms (0.21 g), m.p. 85—86°, $\lambda_{max.}$ 235 and 272infl nm (log 3.44 and 3.19), $\nu_{max.}$ 1 715 (lactone), 1 692 (pivaloyl), and 1 620 cm^{-1} (aromatic and ene) (Found: C, 74.4; H, 7.0%; *M*, 258. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%; *M*, 258).

Although spectroscopic findings showed that the non-crystalline residues from this preparation contained a major quantity of this oxepinone it could not be separated easily; further reactions with it were therefore conducted without separation, as follows. 3-Pivaloylcoumarin (1.5 g) was treated with diazoethane (*ca.* 1.5 g) as before, and after 30 min volatile materials were removed *in vacuo* and the oily product was kept in ether (50 ml) for 3 h, after which no further evolution of nitrogen was observed. To this solution at 0 °C was added diazoethane (*ca.* 2 g) in ether (200 ml), and after 30 min all volatile materials were again removed *in vacuo* at 0 °C. This time the residue was semi-solid, trituration with cold pentane giving 3,3a,4,10a-*tetrahydro*-3,4-*dimethyl*-10a-*pivaloyl*[1]*benzoxepino*[3,4-c]*pyrazol*-10-*one* (IXa) as a powder (0.91 g), m.p. 125—127° (decomp.), $\nu_{max.}$ 1 750 (lactone), 1 697 (pivaloyl), 1 605 (aromatic), and 1 550 cm^{-1} (azo) (Found: C, 68.7; H, 6.9; N, 8.9%. $C_{18}H_{22}N_2O_3$ requires C, 68.8; H, 7.0; N, 8.9%). The same compound was produced quantitatively by adding diazoethane in ether to the benzoxepin (VIb) in the same solvent.

The combined mother liquors and washings from isolation of the pyrazoline (IXa) were filtered through alumina and concentrated giving an oil which deposited a solid, more of which was isolated by chromatographing the residue on silica from ether–light petroleum (1 : 19). The combined solids (0.78 g) were crystallised from pentane giving 4-*ethyl*-3-*pivaloylcoumarin* (IIIc) as needles, m.p. 69°, $\lambda_{max.}$ 225, 278, and 315 nm (log ε 3.63, 3.98, and 3.83), $\nu_{max.}$ 1 720sh, 1 700, and 1 690sh cm^{-1} (lactone and ketone) (Found: C, 74.4; H, 6.9%; *M*, 258. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%; *M*, 258).

Thermolysis of the Benzoxepinopyrazole (IXa).—When the benzoxepinopyrazole (IXa) (0.5 g) in benzene was heated under reflux with exclusion of moisture for 15 h and the solvent removed, an oil remained which was separated into its components by chromatography on silica (47 g). Ether–light petroleum (1 : 19) eluted 1,1a,8,8a-*tetrahydro*-1,8-*dimethyl*-1a-*pivaloylcyclopropa*[c][1]*benzoxepin*-2-*one* (XII), an oil which separated slowly from pentane as prisms (0.034 g), m.p. 86—88°, $\nu_{max.}$ (mull) 1 738 (lactone) and 1 688 cm^{-1} (pivaloyl) (Found: *M*, 286.157 86. $C_{18}H_{22}O_3$ requires 286.156 89). Further elution with ether–light petroleum (1 : 9) gave 5,6-*dihydro*-5,6-*dimethyl*-3-*pivaloyl*-1-*benzoxocin*-2-*one* (XIa), which crystallised from pentane as prisms (0.09 g), m.p. 69°, $\lambda_{max.}$ 233, 262, and 270 nm (log ε 3.48, 2.99, and 2.91), $\nu_{max.}$ (mull) 1 720 (lactone) and 1 680 cm^{-1} (pivaloyl) (Found: C, 75.6; H, 7.8%; *M*, 286. $C_{18}H_{22}O_3$ requires C, 75.5; H, 7.7%; *M*, 286). Finally, extended elution with the same solvent mixture supplied 4-*ethyl*-5-*methyl*-3-*pivaloyl*-1-*benzoxepin*-2(5H)-*one* (X) as an oil (0.32 g) that behaved chromatographically and spectroscopically as a single substance but failed to crystallise; it had $\lambda_{max.}$ 242, 267, 273, and 315infl nm (log ε 3.49, 3.34, 3.35, and 2.78), $\nu_{max.}$ (film) 1 705br (lactone and ketone) and 1 625 cm^{-1} (aromatic and ene) (Found: *M*, 286.157 14. $C_{18}H_{22}O_3$ requires *M*, 286.156 89).

3-(4-*Methylphenylsulphonyl*)*coumarin and Diazoethane*.—A solution of 2-hydroxybenzaldehyde (3.0 g) and methyl 4-methylphenylsulphonylacetate [30] (6.0 g) in methanol (10 ml) containing piperidine (3 drops) deposited a white solid during 3 h. After that, the solvent was removed and the residue crystallised from acetic acid to furnish 3-(4-methylphenylsulphonyl)coumarin (XIIIa) as needles (5.9 g), m.p. 220° (lit.,[31] 221°).

To 3-(4-methylphenylsulphonyl)coumarin (1.0 g) in tetrahydrofuran (100 ml) at 0 °C was added diazoethane (*ca.* 1.0 g) in ether (50 ml). After 1 h at 0 °C, the solution was concentrated under reduced pressure without allowing rise in temperature. Attempts to remove all the solvent always led to decomposition of the product, but dilution with chilled ether and cooling (acetone–solid carbon dioxide) gave a microcrystalline solid that was purified for analysis by dissolving it in chilled chloroform (ethanol-free), filtering, and reprecipitating it with cold pentane. This gave 1,9a-*dihydro*-1-*methyl*-3a-(4-*methylphenylsulphonyl*)[1]*benzopyrano*[3,4-c]*pyrazol*-4(3aH)-*one* (XIV) as a powder, m.p. *ca.*

[29] M. W. Rathke and J. Deitch, *Tetrahedron Letters*, 1971, 2953.
[30] D. J. Pasto, D. McMillan, and T. Murphy, *J. Org. Chem.*, 1965, **30**, 2688.
[31] J. Troger and F. Bolte, *J. prakt. Chem.*, 1922, **103**, 163.

85° (decomp.), $\nu_{max.}$ 1 735 (lactone), 1 540 (azo), and 1 315 and 1 150 cm^{-1} (sulphone) (Found: C, 60.6; H, 4.5; N, 7.6. $C_{18}H_{16}N_2O_4S$ requires C, 60.7; H, 4.5; N, 7.9%).

Because of the instability of this pyranopyrazole, work with it was conducted with the crude oily material and not with the solid. Thermolysis of the oil (from 1 g of coumarin) in refluxing benzene (50 ml) was effected with complete exclusion of moisture. After 30 min the product was isolated and chromatographed on silica (115 g) from ether–light petroleum (1 : 4) initially. This removed traces of oily material, which were discarded. Ether–light petroleum (1 : 3) then eluted material which separated from ether giving *5-methyl-3-(4-methylphenylsulphonyl)-1-benzoxepin-2(3H)-one* (XVI) as prisms (0.24 g), m.p. 178—180° (decomp.), $\lambda_{max.}$ 248 nm (log ε 3.85), $\nu_{max.}$ 1 770 (lactone), 1 625 (aromatic and ene), and 1 327 and 1 148 cm^{-1} (sulphone) (Found: C, 65.75; H, 5.1; S, 9.9%; *M*, 328. $C_{18}H_{16}O_4S$ requires C, 65.85; H, 4.9; S, 9.8%; *M*, 328). Finally, elution with ether–light petroleum (1 : 1) supplied a substance purified from ethanol to give *4-ethyl-3-(4-methylphenylsulphonyl)coumarin* (XV) as needles (0.67 g), m.p. 136—138°, $\lambda_{max.}$ 284 and 327 nm (log ε 3.82 and 3.11), $\nu_{max.}$ 1 730 (lactone) and 1 340 and 1 155 cm^{-1} (sulphone) (Found: C, 65.6; H, 4.8; S, 9.6%; *M*, 328. $C_{18}H_{16}O_4S$ requires C, 65.9; H, 4.9; S, 9.8%; *M*, 328).

3-(4-Methylphenylsulphinyl)coumarin (XIIIb).—The solid formed by a mixture of 2-hydroxybenzaldehyde (3.5 g), methyl 4-methylphenylsulphinylacetate [32] (7.0 g), and piperidine (1 ml) held at 80 °C for 20 min was collected and purified from benzene–hexane giving *3-(4-methylphenylsulphinyl)coumarin* as fine needles (7.2 g), m.p. 208—209°, $\nu_{max.}$ 1 725 (lactone) and 1 052 cm^{-1} (sulphoxide) (Found: C, 67.4; H, 4.4; S, 11.5%; *M*, 284. $C_{16}H_{12}O_3S$ requires C, 67.6; H, 4.3; S, 11.2%; *M*, 284).

3-Methyl[1]benzopyrano[3,4-c]pyrazol-4(3H)-one (XIXc).—To the foregoing coumarin (1.0 g) in tetrahydrofuran (50 ml) was added diazomethane (*ca.* 2.5 g) in ether (100 ml) at 0 °C. Effervescence was complete after 1 h, and removal of the solvent left a solid which was purified on silica (60 g) by elution with ether–light petroleum (1 : 9) which gave an oil (0.34 g), further elution with ether–light petroleum (1 : 4) giving the *pyranopyrazolone* as needles (0.65 g) (from chloroform–hexane), m.p. 160—162°, $\lambda_{max.}$ 252 and 303 nm (log ε 4.78 and 4.95), $\nu_{max.}$ 1 736 (lactone) and 1 592 cm^{-1} (pyrazole), τ ($CDCl_3$) 2.03 (s, pyrazole 3-H), 2.2—2.8 (mm, ArH), and 5.71 (s, NMe) (Found: C, 65.9; H, 4.1; N, 14.1%; *M*, 200. $C_{11}H_8N_2O_2$ requires C, 66.0; H, 4.0; N, 14.0%; *M*, 200). The oil was oxidised with an excess of 30% hydrogen peroxide in acetic acid and the 4-methylbenzenesulphonic acid produced characterised as the *S*-benzylisothiuronium salt, m.p. 182°.

3-Ethyl-1-methyl[1]benzopyrano[3,4-c]pyrazol-4(3H)-one (XIXb).—The preceding experiment was repeated but with diazoethane (*ca.* 2.5 g) instead of diazomethane. In this case elution with ether–light petroleum (1 : 9) gave the *3-ethyl-1-methylpyrazolone*, which crystallised from chloroform–hexane as needles (0.74 g), m.p. 164°, $\lambda_{max.}$ 252 and 306 nm (log ε 4.73 and 4.72), $\nu_{max.}$ 1 730 (lactone) and 1 590 cm (pyrazole), τ ($CDCl_3$) 2.2—2.8 (mm, ArH), 5.40 (q, *J* 8 Hz, $CH_2{\cdot}CH_3$), 7.40 (s, $CH_3{\cdot}C$:), and 8.52 (t, *J* 8 Hz, $CH_2{\cdot}CH_3$) (Found: C, 68.3; H, 5.4; N, 12.2%; *M*, 228. $C_{13}H_{12}N_2O_2$ requires C, 68.4; H, 5.3; N, 12.3%; *M*, 228). Further elution with ether alone gave *1-methyl[1]benzopyrano[3,4-c]pyrazol-4(3H)-one* (XIXa), separating from benzene–chloroform as a powder (0.05 g), m.p. 225—230° (subl.), $\nu_{max.}$ 3 120 (NH), 1 760 (lactone), and 1 580 cm^{-1} (pyrazole), τ ($CF_3{\cdot}CO_2H$) 1.9—2.4 (mm, ArH) and 7.00 (s, CH_3) (Found: C, 65.9; H, 4.1; N, 14.3%; *M*, 200. $C_{11}H_8N_2O_2$ requires C, 66.0; H, 4.0; N, 14.0%; *M*, 200).

1,1-Dimethyl[1]benzopyrano[3,4-c]pyrazol-4(1H)-one (XX).—2-Diazopropane (*ca.* 0.82 g) in ether (15 ml) was added to 3-(4-methylphenylsulphinyl)coumarin (0.82 g) in tetrahydrofuran (50 ml) at 0 °C. During 15 min the red colour faded and solid separated. This was collected after removing the solvent at 0 °C and freed from an oily contaminant by a brief washing with cold ether. Thus obtained, the *1,1-dimethylpyrazolone* crystallised from chloroform–hexane as faintly green plates (0.56 g), m.p. 240—241° (phase change at 182°), $\lambda_{max.}$ 237, 245, 310, and 340 nm (log ε 4.88, 4.92, 4.79, and 4.81), $\nu_{max.}$ 1 750 (lactone), 1 610 (aromatic), and 1 560 cm^{-1} (azo), τ ($CDCl_3$) 2.2—2.8 (mm, ArH) and 8.29 (s, CH_3) (Found: C, 67.1; H, 4.7; N, 13.2%; *M*, 214. $C_{12}H_{10}N_2O_2$ requires C, 67.3; H, 4.7; N, 13.1%; *M*, 214).

[1]Benzopyrano[3,4-d][1,2,3]triazol-4(3H)-one (XXII).—A rapidly stirred solution of 3-(4-methylphenylsulphinyl)-coumarin (0.82 g) and sodium azide (0.23 g) in dimethylformamide (12.5 ml; distilled from barium oxide) was kept at 95 °C for 5 h under anhydrous conditions. Removal of the solvent under reduced pressure left an oil which was dissolved in water (50 ml) and acidified with hydrochloric acid. The precipitate was purified from ethanol giving the *triazolone* as prisms (0.54 g), m.p. 278—281° (decomp.), $\lambda_{max.}$ 255, 265, 290, and 300 nm (log ε 4.09, 4.07, 3.91, and 3.88), $\nu_{max.}$ 3 150 (NH), 1 760 (lactone), 1 630 (aromatic and ene), and 1 570 cm^{-1} (triazole) (Found: C, 57.7; H, 2.8; N, 22.7%; *M*, 187. $C_9H_5N_3O_2$ requires C, 57.8; H, 2.7; N, 22.5%; *M*, 187).

3-Nitrocoumarin (XXIIIa).—The reported preparation [33] of this compound was not very successful in our hands, but the following modification gave acceptable results. A solution of nitroacetonitrile (6.0 g) and 2-hydroxybenzaldehyde (8.4 g) in ethanol (10 ml) gradually became dark red after the addition of methylamine (0.5 ml). After 10 h the solvent was removed and the viscous residue mixed with methanol (25 ml) and 4N-hydrochloric acid (25 ml) and kept at 80 °C for 1 h. The cooled mixture deposited a black tar which was chromatographed on silica (100 g) from benzene. The main fraction supplied 3-nitrocoumarin as golden plates (from ethanol) (3.3 g), m.p. 143° (lit.,[32] 142°).

3-Nitrocoumarin with Diazoethane for 30 min.—Diazoethane (*ca.* 2.0 g) in ether (200 ml) was added to 3-nitrocoumarin (2.0 g) in tetrahydrofuran (100 ml) at 0 °C and after 30 min volatile materials were removed as in preceding examples. The resulting oil solidified in contact with ether giving *3,3a,4,10a-tetrahydro-3,4-dimethyl-10a-nitro[1]benzoxepino[3,4-c]pyrazol-10-one* (XXIV) as a powder (1.1 g) pure enough for preparative purposes but for analysis reprecipitated from cold tetrahydrofuran by cautious addition of hexane and then obtained as prisms, m.p. 112—115° (decomp.), $\nu_{max.}$ 1 765 (lactone) and 1 570 and 1 330 cm^{-1} (nitro) (Found: C, 56.6; H, 4.9; N, 15.0. $C_{13}H_{13}N_3O_3$ requires C, 56.7; H, 4.8; N, 15.3%).

The mother liquors deposited a further crop of the pyrazoline but as a mixture with another compound which was purified by recrystallisation from tetrahydrofuran–hexane and identified as *1,9b-dihydro-1-methyl[1]benzopyrano[3,4-c]-isoxazol-4-one 3-oxide* (XXVII), forming cream prisms (0.03

[32] W. J. Leonard and C. R. Johnson, *J. Org. Chem.*, 1962, **27**, 282.

[33] H. Junek and W. Wilfinger, *Monatsh.*, 1970, **101**, 1123.

g), m.p. 166°, $\nu_{max.}$ (mull) 1 740 (lactone), 1 625 (aromatic and nitrone), and 1 142 cm^{-1} (nitrone) (Found: *M*, 219.053 30. $C_{11}H_9NO_4$ requires *M*, 219.053 15). The mass spectrum showed strong peaks at *m/e* 203.058 94 (indicative of loss of one oxygen atom; $C_{11}H_9NO_3$ requires *m/e* 203.058 24) and 201.041 31 (indicative of loss of H_2O; $C_{11}H_7NO_3$ requires *m/e* 201.042 24).

The combined mother liquors from the above separations gave material which, when recrystallised from ether, gave 4-*ethyl*-3-*nitrocoumarin* (XXIIIb) as pale yellow needles (0.27 g), m.p. 113°, $\lambda_{max.}$ 282 and 317 nm (log ε 4.02 and 3.74), $\nu_{max.}$ (KBr) 1 730 (lactone) and 1 540 and 1 345 cm^{-1} (nitro) (Found: C, 60.0; H, 4.2; N, 6.4%; *M*, 219. $C_{11}H_8NO_4$ requires C, 60.3; H, 4.1; N, 6.4%; *M*, 219).

The material still left in the mother liquors was chromatographed on silica (180 g). Elution with ether–light petroleum (1 : 9) removed a yellow oil (discarded); then elution with the same solvents (1 : 4) gave 1,1a,8,8a-*tetrahydro*-1,8-*dimethyl*-1a-*nitrocyclopropa*[c][1]*benzoxepin*-2-*one* (XXVI), which formed prisms (from hexane) (0.17 g), m.p. 72°, $\lambda_{max.}$ 232 nm (log ε 3.49), $\nu_{max.}$ 1 758 (lactone) and 1 530 and 1 350 cm^{-1} (nitro) (Found: C, 63.2; H, 5.6; N, 5.6%; *M*, 247. $C_{13}H_{13}NO_4$ requires C, 63.2; H, 5.3; N, 5.7%; *M*, 247).

Continued elution gave 1a,7b-*dihydro*-1-*methyl*-1a-*nitrocyclopropa*[c][1]*benzopyran*-2(1H)-*one* (XXV) as needles (from ether–hexane) (0.3 g), m.p. 111—112°, $\lambda_{max.}$ 237 and 275sh nm (log ε 3.54 and 3.03), $\nu_{max.}$ 1 760 (lactone) and 1 545 and 1 350 cm^{-1} (nitro) (Found: C, 60.1; H, 4.3; N, 6.2%; *M*, 219. $C_{11}H_9NO_4$ requires C, 60.3; H, 4.1; N, 6.4%; *M*, 219).

Elution was completed with ether–hexane (1 : 1) and furnished a second crop (0.27 g; total yield 27%) of 4-ethyl-3-nitrocoumarin.

Thermolysis of the Nitro-oxepinopyrazole (XXIV).—The oxepinopyrazole (0.28 g) was heated in refluxing benzene (10 ml) with exclusion of oxygen and moisture. After 5 h the product, a yellow oil, was separated by preparative t.l.c. (3 plates) with ether–light petroleum (1 : 4) for development. The major band was extracted with chloroform and supplied the nitrocyclopropabenzoxepin (XXVI) (0.18 g). The rest of the material was chromatographically complex but the n.m.r. spectrum showed that no olefinic product was present. Similar thermolyses with acetone or tetrahydrofuran as solvent gave similar results.

3-*Nitrocoumarin with Diazoethane for* 1.5 *h*.—The interaction of diazoethane (*ca.* 2.5 g) with 3-nitrocoumarin (1.0 g) was conducted as before but terminated after 1.5 h by removal of volatile materials. The product crystallised from ether giving 3,3a,4,10a-*tetrahydro*-3,3′,4-*trimethyl*-10a-*nitro*-[1]*benzoxepino*[3,4-c]*pyrazole*-10-*spiro*-2′-*oxiran* (XXX) as silvery plates (0.42 g), m.p. 140—142°, $\lambda_{max.}$ (tetrahydrofuran) 260, 266, 273, and 327 nm (log ε 3.24, 3.25, 3.15, and 2.49), $\nu_{max.}$ 1 550 and 1 345 cm^{-1} (nitro) (Found: C, 59.4; H, 5.7; N, 13.7%; *M*, 303. $C_{15}H_{17}N_3O_4$ requires C, 59.4; H, 5.7; N, 13.9%; *M*, 303).

The same compound resulted from the interaction of diazoethane and the pyrazolone (XXIV) in tetrahydrofuran–ether at 0 °C, but there was almost no reaction between the pyrazolone and either diazomethane or 2-diazopropane during 2 h.

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