Reactions between 3-Nitrochromone and Diazoalkanes; Michael Additions catalysed by Diazoalkanes as Nitrogen Bases

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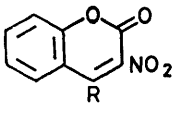
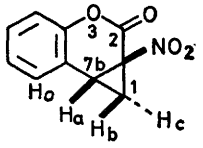
3-Nitrochromone with diazomethane rapidly gives a derivative (4) of cyclopropa[*b*][1]benzopyran-7-one which reacts readily with water or alcohols to give 3,4-dihydro-2-hydroxy-4-nitro-1-benzoxepin-5(2*H*)-one or its ethers. The alcohol is maintained in a particular conformation (9) by hydrogen bonding between the hydroxy- and nitro-groups that makes enolisation impossible, but the ethyl ether (8c) enolises and is easily methylated. With 2-diazopropane the reaction of 3-nitrochromone is extremely vigorous; a derivative (13) of cyclopropa[*b*][1]-benzopyran-7-one is again formed but reacts slowly with ethanol and the ring fission occurs in a different sense so that 2-(1-ethoxy-1-methylethyl)-3-nitrochroman-4-one (14) is formed under what is thought to be stereoelectronic control. With diazoethane the reaction of 3-nitrochromone is more complex and only 2-ethyl-3-nitrochromone (3b) was characterised. If 3-nitrochromone is treated with a diazoalkane in trichloromethane containing ethanol, one of the products (up to 17%) is formed by the Michael addition of the ethanol to the chromone followed by etherification of the resulting enol (17a). In these additions the diazoalkane is regarded as acting as a catalytic nitrogen base.

DIAZOMETHANE rapidly methylates the 4-position in 3-acetylcoumarin and related compounds [1,2] but, as noted briefly already,[3] it converts 3-nitrocoumarin (1a) into the cyclopropane derivative (2) instead of the methylated product (1b). Diazoethane induces a more complex reaction whatever the activating group, and it converts 3-nitrocoumarin into a mixture of the ethyl derivative (1c), a cyclopropane derivative, and other products.[4]

The reasons underlying cyclopropane formation have



(1) a; R = H
b; R = Me
c; R = Et



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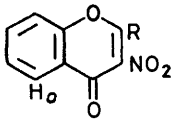
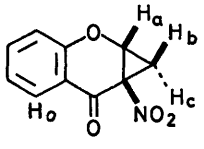


(3) a; R = H
b; R = Et



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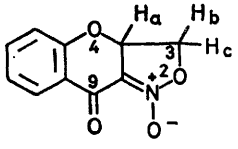
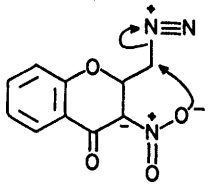


(5)

been discussed elsewhere [3] and predict cyclopropane formation from diazomethane and 3-nitrochromone (3a). 3-Nitrochromone [5] does give mainly the cyclopropa[1]-benzopyran (4) although a little of the isoxazoline oxide (5) is also produced. No pyrazoles or pyrazolines were found such as Russian workers [6] report from some related reactions. The nature of the isoxazoline oxide was first indicated by the i.r. spectrum which showed, instead of



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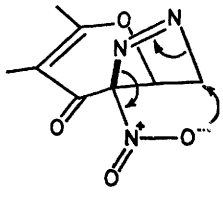


(7)

bands for a nitro-group, bands appropriate to *N*-oxides [7] (1 282 and 950 cm^{-1}) along with a band at 1 685 cm^{-1} indicative of a conjugated carbonyl group. The mass spectrum strongly supported the *N*-oxide formulation because it contained a very strong peak corresponding to the loss of one oxygen atom from the molecular ion. In the ^1H n.m.r. spectrum the X part of an ABX spin system resonates at a very low field (δ 6.1) due, according to structure (5), to conjugation with immonium nitrogen. *N*-Oxides have been noted before in similar reactions; [4] they might arise from intervention by a zwitterion such as (6) formed either in competition with cycloaddition or, after cycloaddition, by ionisation of the adduct. Ionisation might not be necessary since models indicate that the molecule can be constrained into a conformation (7) suitable for the elimination of nitrogen by an electrocyclic mechanism.

Structure (4) for the cyclopropabenzopyran was established by the i.r. spectrum, which showed bands typical of benzoyl carbonyl and of nitro-groups, and by the n.m.r. spectrum (Table 1). These findings refer to the *crude* product (*i.e.* containing the *N*-oxide) because the sensitivity of the compound made its purification too difficult. With water, whether in damp air or on chromatographic columns, *etc.*, the cyclopropabenzopyran reacts smoothly, opening the small ring and giving the 2-hydroxy-1-benzoxepin (8a). At first, the nature of this compound was in doubt, since i.r. evidence for hydroxy-

groups was lacking and the carbonyl band occurred at 1 737 cm^{-1}, a frequency that seemed far too high to be attributed to a conjugated carbonyl group. On the other hand the n.m.r. spectrum (Table 2) clearly required the presence of a $CH_a{\cdot}CH_bH_c{\cdot}CH_d$ grouping since double irradiation experiments proved that H_a and H_d both interact with H_b and H_c but not with each other. Thus we deduced the presence of the seven-membered ring in (8a). Models then showed that the unusual i.r. spectrum could easily be accommodated if the compound were held in conformation (9) by strong hydrogen bonding between the hydroxy- and nitro-groups,[8] in which case the carbonyl group would be rotated well out of co-planarity with the benzene ring and therefore out of conjugation. It is also important that this conformation explains why no ready enolisation is observed, for the enol would disobey Bredt's rule. Moreover, simply shaking the compound with deuterium oxide effected no replacement of the hydroxy-protons as in other cases of very strong hydrogen bonding.[9] The resonances from the hydroxy-proton and the active proton H_d were therefore identified by using deuterium oxide instead of water to open the cyclopropane ring giving (8b). The hydroxylic proton resonates at δ 4.75, rather a high field for one that is considered to be strongly hydrogen bonded, and so we place the hydroxy-group over the benzene ring where it will be shielded. This completes the derivation of conformation (9).

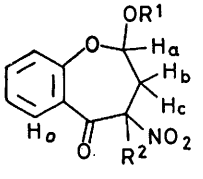
Nucleophilic opening of the cyclopropane ring is well known when activating groups are present.[10] The cyclopropane ring of (4) can also be opened with ethanol or t-butyl alcohol giving the ethers (8c) and (8d), respectively. These compounds were awkward to study because enolisation soon occurred in solutions of the crystalline, ketonic form; nevertheless, the n.m.r. spectrum of the ether (8d) clearly showed that the structure was the same as in the alcohol (8a) but with a different configuration/conformation. On general grounds the large ring is considered to be puckered, with the ether and the nitro-substituents both disposed pseudoequatorially, but we have no direct evidence for conformation (10). Another problem with the ethyl ether (8c) is that, as with several other compounds under discussion, the ethoxy-group is attached to a chiral centre making its methylene group diastereotopic and thus complicating its splitting pattern.[11] The situation could be somewhat simplified by treating the ether with diazomethane to convert it into the methyl ether (11) of the enol with an easier n.m.r. spectrum to analyse (Table 2). The major product, however, was the nitronic ester (12) formed by the alternative 'enolisation'; this compound was also unstable and could not be kept for more than a few hours. Only one decomposition product could be identified readily. This was the true enol

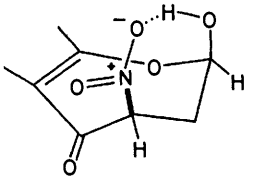
TABLE 1

^1H N.m.r. spectra of compounds related to 1-benzopyran [a]

Compound	Field (MHz)	H_a	H_b	H_c	ArH_o [b]	other ArH	2-OEt CH_2	2-OEt CH_3	other OEt CH_2	other OEt CH_3	OMe	*gem*-Me
(4)	60	4.15 (J_{ab} 6)	2.76 (J_{bc} 10)	2.00 (J_{ac} 8.5)	7.98 (dd)	7.0—7.8 (mm)						
(5)	60	6.10 (J_{ab} 7.5)	5.96 (J_{bc} 18)	4.71 (J_{ac} 9)	8.05 (dd)	7.1—7.9 (mm)						
(13)	220	4.91			7.97 (dd)	7.58 7.1 (2 H, mm)						1.15, 1.24
(14)	220	4.88 (J_{ab} 8.3)	5.60 (J_{ab} 8.3)		7.91 (dd)	7.55 (t) 7.10 (t) 7.01 (d)			3.34 (q, J 7)	0.97 (t, J 7)		1.35, 1.40
(17b)	220	6.28			7.79 (dd)	7.48 7.1 (2 H, mm)	3.87 (mm)	1.21 (m)			4.13	
(17c)	220	6.28			7.80 (dd)	7.46 (m) 7.13 (2 H, mm)	3.88 (mm)	1.21 (m)	4.13 [c] 4.54 [c]	1.17 [c]		

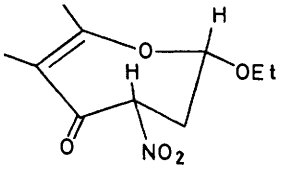
[a] In $CDCl_3$ at *ca.* 25 °C. Relative intensities are those required by the assignments and are not shown where there is no ambiguity. Coupling constants (Hz) are given in parentheses. [b] Coupling constants (first-order) remained close to 8 and 1.5 Hz. [c] $J_{AX} = J_{BX} = 7$; J_{AB} *ca.* 16 Hz.





(8) a; $R^1 = H, R^2 = H_d$
b; $R^1 = R^2 = D$
c; $R^1 = Et, R^2 = H_d$
d; $R^1 = Bu^t, R^2 = H_d$

(9)



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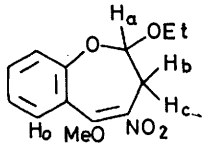

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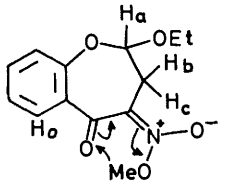


(12)

ether (11) which we take as a (very weak) indication that the nitronic ester has the configuration in (12) which allows the isomerisation to be explained as an easy intramolecular shift of the methyl group.

methylene chemical shift permits only an ether grouping). As usual, the i.r. spectrum evidences the conjugated ketonic (not ester) group and the nitro-group. The compound is readily kept because, in contrast to

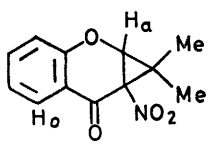
TABLE 2

^{1}H N.m.r. spectra of compounds derived from 1-benzoxepin [a]

Compound	Field (MHz)	H_a	H_b	H_c	H_d	ArH_o [b]	other ArH		OH, OMe, or Bu^{t}O	2-OEt CH_2	2-OEt CH_3
(8a)	220	5.85 [c] (m)	2.80 (m)	2.80 (m)	4.75 [c] (m)	7.99 (dd)	7.62 (m) 7.07 (m)	7.25 (m)	4.75 [d]		
(8b)	220	5.89 ($J_{ab} = J_{ac} = 4.5$; J_{bc} = ?)		2.79		8.02 (dd)	7.64 (m) 7.07 (m)	7.25 (m)			
(8c)	100	~5.5 (m)	~2.8 (m)	~2.8 (m)	~5.5 (m)					3.75 4.01 (mm)	1.21 (m)
(8d)	100; 220	5.80 (dd, J 7, 10.5)	~2.95 (m)	~2.95 (m)	5.25 (dd, J 5, 8)	7.91 (dd)	7.58 (m) 7.09 (m)	7.22 (m)	1.26		
(11)	220	5.65 (J_{ab} 10.5)	2.23 (J_{bc} 15)	3.32 (J_{ac} 5)		7.49 (dd)	7.28	7.13 (d, J 8)	3.76	3.76 4.13 (mm)	1.29 (t, J 7)
(12)	60	5.39 (J_{ab} 9)	2.55 (J_{bc} 15.5)	3.37 (J_{ac} 4.5)		7.80 (dd)	7.6—6.9 (mm)		3.85	~3.9 (m)	1.30 (m)

[a] In $CDCl_3$ at *ca.* 25 °C. Relative intensities are those required by the assignments. First-order coupling constants (Hz) are given in parentheses. [b] Coupling constants (first-order) remained close to 8 and 1.5 Hz. [c] Collapsed to singlet when H_aH_b protons were saturated. [d] Shaking with D_2O does not remove this H signal; see text.

The more nucleophilic diazoalkane, 2-diazopropane, reacts vigorously with 3-nitrochromone even at −78 °C. Only the major product was identified. Although assigned the cyclopropane structure (13) on the basis of



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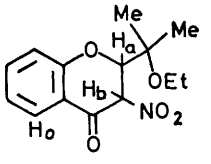
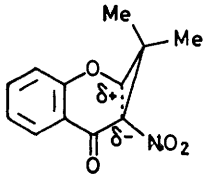


(14)

i.r. evidence for nitro and conjugated carbonyl groups, and n.m.r. evidence (Table 1) for two independent methyl groups and one methine proton, the compound is much more stable than its counterpart (4) and reacts fully with ethanol only during 15 h at 76 °C. Moreover, the small ring opens in a different sense giving the chromanone derivative (14). The n.m.r. spectrum (Table 1) provides



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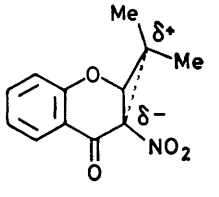
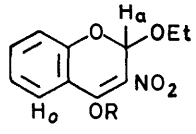


(16)

evidence for two independent methyl groups, two methine protons forming an AB spin system, and an ethoxy-group neither attached to a chiral centre (the splitting is simple A_2X_3) nor forming an ester component (the

the corresponding 1-benzoxepin (8c), it does not enolise easily. In the smaller (pyran) ring, enolisation would introduce another sp^2 atom and considerably increase the ring (angle) strain.

The relative stability of the dimethyl compound (13) is expected because of the *gem*-dialkyl effect which stabilises small rings,[12] but the change in the direction of ring opening is interesting. We seek to explain this by considering an incipient ionisation in the bonds concerned. Diagram (15) places a partial positive charge adjacent to an oxygen atom which might be expected to



(17) a; R = H
b; R = Me
c; R = Et

stabilise it. Nevertheless, models discount extensive delocalisation because the bond being broken is in the wrong plane for interaction with the p–π orbitals on oxygen. In diagram (16), on the other hand, the situation is reversed. Although two methyl groups usually have a much weaker stabilising effect than one oxygen atom, they can interact fully with the growing positive charge. In this way we rationalise both the difference in rates of reaction and the difference in the regiospecificity.

For the reaction with diazomethane, it is convenient

to dissolve the nitrochromone in trichloromethane, but this must be free from ethanol. If not, the ethanol adds to the chromone during the diazoalkane reaction and the product, the enol (17a) (not isolated) is then alkylated further giving the methyl ether (17b). This can be isolated in up to 17% yield, and its structure is clear from the facts that it possesses no carbonyl absorption in the infrared but retains a characteristic nitro-absorption, while the n.m.r. spectrum includes lines appropriate to an ethoxy-group, a methoxy-group, and one methine proton of acetal type (Table 1). Ethanol does not add to 3-nitrochromone without assistance; indeed, it is a good solvent for the recrystallisation of the chromone. If a trace of base is added, however, a rapid reaction ensues, as would be expected since the 3-nitrochromone should be a good Michael acceptor. Unfortunately, the product proved to be intractable, probably because of ready enolisation in either direction and ring opening and other reactions. Since some adventitious base might have been responsible when the diazomethane was employed the usual reagent solution was prepared but the diazomethane was removed in a current of nitrogen. The residual solution had no effect upon a solution of the chromone in trichloromethane, so we believe the diazomethane itself to be the catalytic (nitrogen) base as in examples we have discussed elsewhere.[13]

A similar alkylation with diazoethane gave the ethyl ether (17c) containing two ethoxy-groups. One has a spin pattern blurred by attachment to the chiral centre at position 2 as in the other examples, but the second at position 4 shows methylene protons widely separated (Table 1). This cannot be attributed to the rather distant chiral centre and must indicate a substantial degree of hindrance to rotation. In other respects the alkylation seemed very complex and the only other product obtained in a pure state was 2-ethyl-3-nitrochromone (2b) in 37% yield. Here there is some similarity to the action of diazoethane upon 3-nitrocoumarin, which also effects substantial alkylation (to 4-ethyl-3-nitrocoumarin; 27%) at the expense of cyclopropane formation as well as inducing several other reactions.[4]

EXPERIMENTAL

U.v. spectra were determined for *ca.* 10^{-3} M-solutions in ethanol. Molecular weights were determined mass spectroscopically. Light petroleum refers to the fraction of b.p. 60—80 °C. Ethereal diazomethane and diazoethane were kept for 2 h over potassium hydroxide pellets and redistilled twice before use.

Reaction of 3-Nitrochromone with Diazomethane.—A solution of 3-nitrochromone (0.8 g) in ethanol-free trichloromethane (25 ml) at 21 °C was treated with diazomethane (*ca.* 0.4 g) in ether (150 ml). Evolution of nitrogen was brisk and after 0.5 h no starting chromone could be detected. Removal of the volatile materials without the application of heat left an unstable yellow oil (1.01 g) consisting mainly of 1a,7a-dihydro-7a-nitrocyclopropa[*b*][1]benzopyran-7(1*H*)-one (4), $\nu_{max.}$ (film) 1 690 (benzoyl C:O), 1 610 (aromatic), and 1 550 and 1 340 cm^{-1} (nitro) (Found: *M*, 205. Calc. for $C_{10}H_7O_4$: *M*, 205). The n.m.r. spectrum is included in Table 1.

The yellow oil in freshly purified tetrahydrofuran (30 ml) was mixed with water (100 ml) and brought to reflux for 1.5 h then cooled and poured into trichloromethane (200 ml). The organic phase was washed with water and saturated brine and then dried ($MgSO_4$) and concentrated to another yellow oil (0.87 g). This was chromatographed on a column of silica (100 g) with elution by benzene–light petroleum (25 : 1 v/v) to remove an oil (0.01 g) which was discarded and then a solid which, crystallised from ethanol–hexane, gave 3,4-*dihydro*-2-*hydroxy*-4-*nitro*-1-*benzoxepin*-(2H)-*one* (8a) as faintly yellow plates (0.48 g), m.p. 63 °C, $\lambda_{max.}$ 238 and 298 nm (log ε 3.71 and 3.22), $\nu_{max.}$ 1 737 (out-of-plane C:O), 1 610 (aromatic), and 1 545 and 1 300 cm^{-1} (nitro) (Found: C, 53.9; H, 4.1; N, 6.4%; *M*, 223. $C_{10}H_9NO_5$ requires C, 53.8; H, 4.1; N, 6.3%; *M*, 223). Further elution with the same solvent produced an intermediate fraction (0.06 g) consisting of the oxepinone and another material which was obtained pure from later fractions and when crystallised from benzene–hexane supplied 3,3a-*dihydro*-9-*oxo*-9H-[1]*benzopyrano*[3,2-c]-*isoxazoline* 1-*oxide* (5) as yellow prisms (0.06 g), m.p. 183—184 °C, $\lambda_{max.}$ 302 and 345 nm (log ε 3.86 and 3.45), $\nu_{max.}$ (KBr) 1 685 (conj. C:O), 1 605 (aromatic), and 1 282 and 950 cm^{-1} (*N*-oxide), δ ($CDCl_3$) 4.55—5.20 (2 N, mm, OC*H*$_2$-CH), 6.10 (1 H, m, OCH$_2$C*H*), 7.0—7.8 (3 H, mm, ArH), and 8.03 (1 H, m, ArH at 8-position) (Found: *m/e* 205.035 27. $C_{10}H_7NO_4$ requires *M*, 205.037 50. Found: *m/e* 189.042 86. $C_{10}H_7NO_3$ requires $M^{\cdot+}$ — O, 189.042 59. Found: *m/e* 187.026 91. $C_{10}H_5NO_2$ requires $M^{\cdot+}$ — H_2O, 187.026 94).

3-Nitrochromone was again treated with diazomethane as described above but the resulting yellow oil was heated under reflux with deuterium oxide (10 ml) instead of water. The products were isolated as before giving [4-^{2}H]-3,4-*dihydro*-2-[^{2}H]*hydroxy*-4-*nitro*-1-*benzoxepin*-5(2H)*one* (8b), crystallising from ethanol–hexane as plates (0.60g), m.p. 63 °C, $\lambda_{max.}$ 238 and 297 nm (log ε 3.88 and 3.49), $\nu_{max.}$ (KBr disc) 1 740 (non-conj. C:O), 1 610 (aromatic), and 1 535 and 1 298 cm^{-1} (nitro) (Found: *M*, 225. $C_{10}D_2H_7NO_5$ requires *M*, 225). The isoxazole oxide (5) was also found in later fractions.

Reactions of the Cyclopropabenzopyran (4) *with Alcohols.*—(i) *With ethanol.* To a solution of diazomethane (*ca.* 1.0 g) in ether (200 ml) at 0 °C was added 3-nitrochromone (3 g) in nitromethane (50 ml) so that addition was complete after *ca.* 15 min, the flask being swirled occasionally. During another 1.5 h at 0 °C slow evolution of nitrogen was observed. The volatile materials were then removed without the use of heat and the residual oil subjected to reduced pressure (*ca.* 20 mmHg) at 50 °C. The cyclopropabenzopyran (4), left as a brownish oil, was heated with ethanol (50 ml) under reflux for 1 h. Removal of solvents left an oil which was chromatographed on silica (300 g) from benzene–ether (25 : 1 v/v) giving fractions that separated from light petroleum to furnish 2-*ethoxy*-3,4-*dihydro*-4-*nitro*-1-*benzoxepin*-5(2H)-*one* (8c) as needles (2.8 g), m.p. 86—87 °C, $\lambda_{max.}$ 250, 302, and 360 nm (log ε 3.82, 3.35, and 3.58), $\nu_{max.}$ (KBr) 1 685 (conj. C:O), 1 600 (aromatic), 1 550, 1 330, and 1 310 cm^{-1} (nitro) (Found: C, 57.3; H, 5.1; N, 5.5%; *M*, 251.077 52. $C_{12}H_{13}NO_5$ requires C, 57.4; H, 5.2; N, 5.6%; *M*, 251.079 37).

(ii) *With t-butyl alcohol.* Experiment (i) was repeated but

with t-butyl alcohol (50 ml) instead of ethanol and with a reflux time of 1.5 h. The product crystallised from ethanol giving 3,4-*dihyro*-4-*nitro*-2-*t*-*butoxy*-1-*benzoxepin*-5(2H)-*one* (8d) as plates (1.1 g), m.p. 111—112 °C, $\lambda_{max.}$ 251, 305, and 360 nm (log ε 3.89, 3.42, and 3.63), $\nu_{max.}$ (KBr) 1 690 (conj. C:O), 1 597 (aromatic), 1 558, 1 327, and 1 305 cm^{-1} (nitro) (Found: C, 60.3; H, 6.1; N, 5.0%; *M*, 279.112 98. $C_{14}H_{17}NO_5$ requires C, 60.2; H, 6.1; N, 5.0%; *M*, 279.110 66).

Methylation of Benzoxepin (8c).—Diazomethane (*ca.* 0.03 g) in ether (100 ml) was added to the ketone (8c) (0.25 g) in ethanol-free trichloromethane (15 ml) at 0 °C. Reaction appeared to be complete after *ca.* 0.5 h and volatile materials were then removed without use of heat. The residual oil was purified by chromatography on silica (trichloromethane as eluant) to afford 2-*ethoxy*-2,3-*dihydro*-5-*methoxy*-4-*nitro*-1-*benzoxepin* (11) which separated from pentane as yellow plates (0.05 g), m.p. 74—75 °C, $\lambda_{max.}$ 235 and 302 nm (log ε 3.83 and 3.93), $\nu_{max.}$ (KBr) 1 610 and 1 596 (ene and aromatic), and 1 490 and 1 332 (nitro) (Found: C, 58.8; H, 5.7; N, 5.4%. $C_{13}H_{15}NO_5$ requires C, 58.9; H, 5.7; N, 5.3%). A molecular ion was not observed in the mass spectrum (Found: *m/e* 220.060 97. $C_{11}H_{10}NO_4$ requires $M^{\cdot+}$ − OEt, 220.060 98).

Further elution with trichloromethane provided the *methyl* 2,3-*dihydro*-4-*oxo*-3-*nitronate* (12) as an unstable yellow oil (0.09 g), $\lambda_{max.}$ 303 nm (log ε 3.95), $\nu_{max.}$ (KBr) 1 665 (conj. C:O) and 1 600 cm^{-1} (aromatic). The n.m.r. spectrum is given in Table 2. A molecular ion could not be clearly distinguished in the mass spectrum (Found: *m/e* 249.097 84 and 220.071 42. $C_{13}H_{10}NO_3$ requires $M^{\cdot+}$ − O, 249.100 10. $C_{12}H_7O_2$ requires $M^{\cdot+}$ − NOMe, 220.073 55). When kept for a few weeks the oil deteriorated and the products were separated chromatographically on silica (trichloromethane as eluant). Several fractions were obtained but the only recognisable compound (15%), identified in the usual way, was the methoxynitrobenzoxepin (11).

Reaction of 3-*Nitrochromone with* 2-*Diazopropane*.—Diazopropane (*ca.* 0.5 g) in ether (50 ml) and 3-nitrochromone (1.0 g) in ethanol-free trichloromethane (30 ml) were cooled to −70 °C and then mixed; an immediate vigorous reaction ensued. After *ca.* 20 min volatile materials were removed *in vacuo* without heating, to leave a dark oil which was dissolved in trichloromethane and shaken with charcoal to remove tar. The solution was then passed down a column of silica (150 g); trichloromethane eluted 1a,7a-*dihydro*-1,1-*dimethyl*-7a-*nitrocyclopropa*[b][1]*benzopyran*-7-(1H)-*one* (13), separating from pentane–ether as small plates (0.45 g), m.p. 119 °C, $\lambda_{max.}$ 214, 255, and 328 nm (log ε 4.22, 3.95, and 3.43), $\nu_{max.}$ (KBr) 1 675 (conj. C:O), 1 600 and 1 578 (ene and aromatic), and 1 530 and 1 310 cm^{-1} (nitro) Found: C, 62.0; H, 4.6; N, 5.9%; *M*, 233.067 95. $C_{12}H_{11}NO_4$ requires C, 61.8; H, 4.8; N, 6.0%; *M*, 233.068 80). Further slow-moving red fractions were not eluted for examination.

The cyclopropabenzopyran (13) (0.15 g) was kept in refluxing ethanol (30 ml) for 15 h after which no starting material was detected. Isolated in the usual way, the product crystallised from light petroleum to give 2-(1-*ethoxy*-1-*methylethyl*)-3-*nitrochroman*-4-*one* (14) as small yellow plates (0.17 g), m.p. 54 °C, $\lambda_{max.}$ 213, 256, 328, and 388 nm (log ε 3.78, 3.50, 3.11, and 2.84), $\nu_{max.}$ (KBr) 1 700 (benzoyl C:O), 1 605 (aromatic), and 1 560 and 1 302 (nitro) (Found: C, 60.0; H, 6.0; M, 4.9%, *M*, 279.110 86. $C_{14}H_{17}MO_5$ requires C, 60.2; H, 6.1; N, 5.0%; *M*, 279.110 66).

Michael Additions to 3-*Nitrochromone*.—(i) *With diazomethane*. To 3-nitrochromone (0.63 g) in commercial trichloromethane (containing *ca.* 5% ethanol) was added diazomethane (*ca.* 0.30 g) in ether (200 ml) at 21 °C. After *ca.* 0.5 h the starting chromone could no longer be detected and volatile materials were removed *in vacuo* without heating and the residual oil was chromatographed on silica (82 g) [benzene–ether (5 : 1 v/v) as eluant]. The earlier fractions supplied 2-*ethoxy*-4-*methoxy*-3-*nitro*-2H-*chromen* (17b) as an oil (0.14 g) that separated from cool pentane as yellow plates, m.p. 51—52 °C, $\lambda_{max.}$ 240, 308, and 350 nm (log ε 3.66, 3.80, and 3.70), $\nu_{max.}$ (KBr) 1 620 (ene and aromatic), and 1 565 and 1 340 cm^{-1} (nitro) (Found: C, 57.6; H, 5.3; N, 5.8%; *M*, 251.078 68. $C_{12}H_{13}NO_5$ requires C, 57.4; H, 5.2; N, 5.6%; *M*, 251.079 37). Later fractions contained the cyclopropabenzopyran (4) (0.65 g) described above.

(ii) *With diazoethane*. Experiment (i) was repeated using the nitrochromone (1.0 g) but diazoethane (*ca.* 1.0 g) instead of diazomethane. Chromatography was conducted with ethanol-free trichloromethane as eluant, and gave two main fractions. The second of these formed an oil that crystallised from ethanol–light petroleum to give 2-*ethyl*-3-*nitrochromone* (3b) as yellow plates (0.42 g), m.p. 116 °C, $\lambda_{max.}$ 245 and 3.70 nm (log ε 4.06 and 3.78) δ ($CDCl_3$) 1.44 (3 H, t, *J* 7 Hz, CH_2CH_3) 2.87 (2 H, q, *J* 7 Hz, CH_2CH_3), 7.56 (2 H, mm, ArH), 7.80 (1 H, m, ArH), and 8.23 (1 H, dd, *J* 8, 1.5 Hz, H at 5-position), $\nu_{max.}$ (KBr) 1 655, 1 617, and 1 600 (chromone pattern), and 1 522 and 1 370 cm^{-1} (nitro) (Found: C, 60.1; H, 4.2; N, 6.3%; *M*, 219.053 08. $C_{11}H_9NO_4$ requires C, 60.3; H, 4.1; N, 6.4%; *M*, 219.053 15).

The first oily fraction was rechromatographed over Kieselgel 60 (60 g) [ether–light petroleum (1 : 4 v/v) as eluant]. The resulting light yellow oil crystallised from pentane to supply 2,4-*diethoxy*-3-*nitro*-2H-*chromen* (17c) as rough orange crystals (0.25 g), m.p. 56—57 °C, $\lambda_{max.}$ 238, 310, and 350 nm (log ε 3.30, 3.47, and 3.41), $\nu_{max.}$ (KBr) 1 615 (br, ene and aromatic), and 1 560 and 1 535 cm^{-1} (nitro) (Found: C, 59.1; H, 5.7; N, 5.3%; *M*, 265.095 10. $C_{13}H_{15}NO_5$ requires C, 58.9; H, 5.7; N, 5.3%; *M*, 265.095 01). Other fractions were mixtures and were not examined further.

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