Steric Effects in the Ring-expansion of Coumarins by 2-Diazopropane and t-Butyldiazomethane

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3-Cyanocoumarin gives in high yields its 4-isopropyl derivative with 2-diazopropane and its 4-t-butyl derivative with t-butyldiazomethane showing that the 4-alkylation of 3-cyanocoumarin is general and unaffected by bulky substituents on the diazoalkane.

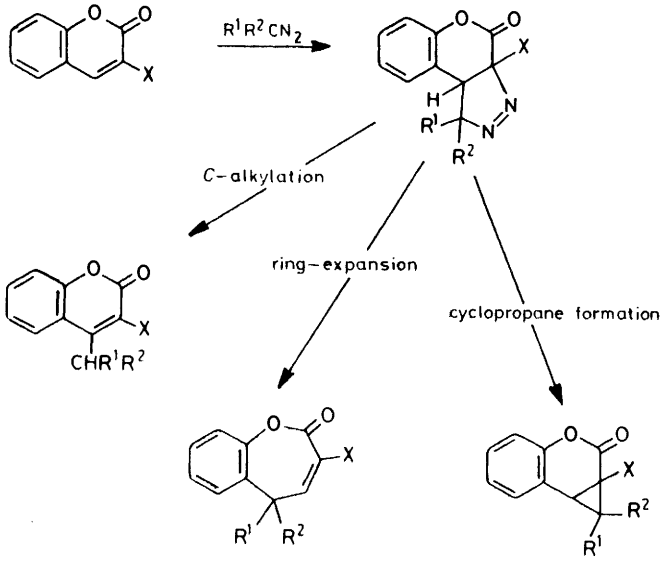
With 2-diazopropane, 3-acetylcoumarin undergoes ring-expansion after which inverse cycloaddition of the diazoalkane leads to 3a-acetyl-3,3a,10,10a-tetrahydro-3,3,10,10-tetramethyl-4*H*-[1]benzoxepino[4,3-*c*]pyrazol-4-one (6a). In the similar reaction with 3-benzoylcoumarin the inverse cycloaddition is slow enough for the intermediate lactone (4b) to be isolated; a cyclopropane derivative is also obtained in low yield.

t-Butyldiazomethane converts both 3-acetylcoumarin and 3-benzoylcoumarin into cyclopropane derivatives, *e.g.* 1a-benzoyl-1-t-butyl-1a,7b-dihydrocyclopropa[*c*][1]benzopyran-2(1*H*)-one (14b), and there is little or no ring-expansion.

It is concluded that although some bulk is required in the diazoalkane to force the pyrazoline into the correct conformation for ring-expansion, too great a bulk is deleterious because collisions divert the reaction into other channels.

A note is added on a ring-contraction (1-benzoxepin to benzofuran derivative) induced by silver nitrate-alumina columns used for chromatography.

THE addition of diazoalkane to coumarins with an electronegative substituent at position 3 produces Δ^1-pyrazolines which lose nitrogen to give products of theoretical and synthetic interest. Elimination of nitrogen may be concerted with hydrogen migration (= alkylation), aryl migration (= ring-expansion), or ring-closure (= cyclopropane formation) (Scheme).[1-3]



SCHEME

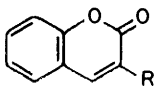
3-Acetylcoumarin (1a) undergoes sequential ring-expansions with diazoethane to give oxepin, oxocin, and oxonin derivatives and this reaction has been developed into a general synthetic method for the ring homologation of cyclic ketones and lactones.[1,4] In contrast, diazomethane simply alkylates 3-acetylcoumarin (1a) which leads us to believe that the bulk of the ethylidene residue forces Δ^1-pyrazolines into a conformation which favours aryl migration.[1,5]

We have, therefore, investigated the effect upon 3-acetylcoumarin (1a) of 2-diazopropane and t-butyldiazomethane in order to find out whether larger groups improve or impair the ring expansion. For comparative purposes 3-cyanocoumarin (1b) and 3-benzoylcoumarin (1c) were also studied.

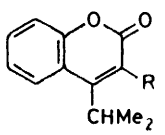
RESULTS AND DISCUSSION

3-Cyanocoumarin has been alkylated by the simplest diazoalkanes, and did not suffer ring-expansion.[2] Similarly, it reacted smoothly with 2-diazopropane at 0 °C to supply the 4-isopropylcoumarin (2a) in quantitative yield, the n.m.r. spectrum confirming the presence of the isopropyl group. A more complex reaction occurred with 3-acetylcoumarin from which was isolated a product (44%) which had been formed from one molecule of the coumarin and two of diazoalkane with loss of one molecule of nitrogen. This suggested that the reaction had proceeded as in the diazoethane series [1] and that the initial adduct (3) had immediately collapsed to give the oxepin derivative (4a) and then added a second molecule of diazoalkane to give the benzoxepinopyrazole (5). However, the thermal stability of the compound and the presence of a proton singlet at τ 4.98 in the ^{1}H n.m.r. spectrum indicated that the adduct was really the alternative benzoxepinopyrazole (6a). The signal for the proton singlet was not removed by D_2O, proving that the compound was not a 2-pyrazoline, and other spectroscopic features were also consistent with the assigned structure. The inverted addition of the diazoalkane is no doubt due to the steric compression of the methyl groups that would occur during the formation of adduct (5). Abnormal additions of 2-diazopropane to highly unsymmetrical alkenes with one activating group have been described previously [6,7] and are theoretically un-

exceptional,[8] but this is the first example of such an addition to an alkene in which the greater regioselectivity associated with two electron-withdrawing groups has been overcome. The inverse mode of addition is a relatively slow process, and with 3-benzoylcoumarin formation of the benzoxepinopyrazole (6b) could be restricted to only 6% or less. By reducing both the temperature and the time of reaction we could also obtain a much simpler reaction mixture containing the intermediate oxepin (4b) (53%) along with the isopropylcoumarin (2b) (23%) and the cyclopropane (7) (12%).



(1) a; R = COMe
b; R = CN
c; R = COPh



(2) a; R = CN
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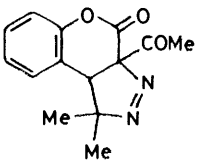

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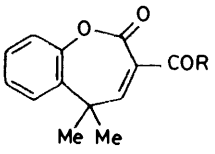
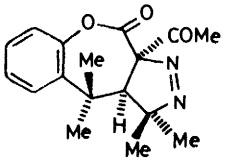


(4) a; R = Me
b; R = Ph



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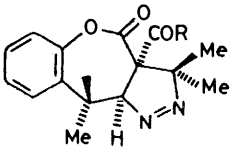
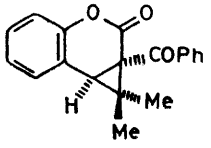


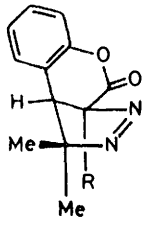
(6) a; R = Me
b; R = Ph



(7)

Thus, both 3-acetylcoumarin and 3-benzoylcoumarin underwent ring-expansion in much better yield with 2-diazopropane than with diazoethane.[1,2] The pyrazolines formed by *cis*-1,3-dipolar cycloaddition to the coumarin may adopt either conformation (8), in which the pyrazoline ring proton is pseudo-equatorial and should therefore favour alkylation (proton migration), or conformation (9), in which the aryl group is pseudo-equatorial and should therefore favour ring-expansion (aryl migration). For both 3-acetylcoumarin and 3-benzoylcoumarin conformation (8) is the less favourable because it contains the equivalent of a 1,3-diaxial interaction between the pseudoaxial methyl group and the acyl group, and models indicate that there is also a steric interaction between the pseudo-equatorial methyl group and an aromatic proton.

As continued ring-expansion with 2-diazopropane was prevented by steric congestion we examined the reaction of oxepin (4b) with the less bulky diazoethane and obtained a quantitative yield of the adduct (10) in which normal addition had occurred. The ^{2}H n.m.r.



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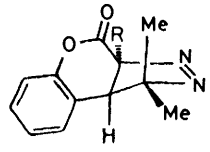
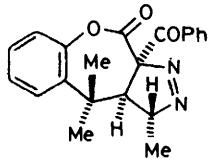


(9)

spectrum establishes the proton sequence CH_3CHCH while the torsional coupling constant of the methine protons indicates that they are trans-diaxial, and it follows that the molecule adopts a conformation in which the secondary methyl group is pseudo-equatorial. This should favour ring-expansion, but thermolysis in benzene gave the ethylated benzoxepin (11) as the major product with the cyclopropane (12) as the minor. So complete an absence of ring-expanded products was unexpected, although models did suggest that expansion would be obstructed by the conflux of several methyl groups.

Thus 2-diazopropane gives improved efficiency only in the initial ring-expansion because the *gem*-dimethyl group it produces prevents any further expansion.



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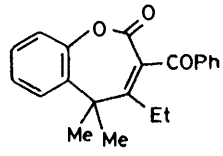

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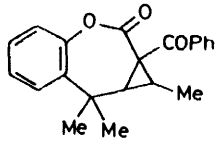

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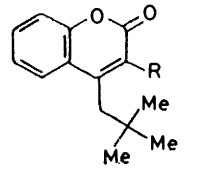
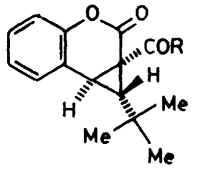


(13) a; R = CN
b; R = Ac

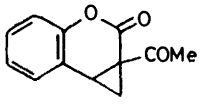
t-Butyldiazomethane reacted much more slowly than the simpler diazoalkanes with 3-cyanocoumarin, but nevertheless gave an excellent yield of the 4-neopentylcoumarin (13a); its large size does not, therefore, impede the very general *C*-alkylation of 3-cyanocoumarins by diazoalkanes.[9] The signal for the methyl

groups in the ^1H n.m.r. spectrum of coumarin (13a) appeared as two peaks (relative intensity 2 : 1) indicating that the rotation of the t-butyl group may be slow on the ^1H n.m.r. time scale, two methyl groups straddling the nearest aromatic proton and the third eclipsing the cyano-group.

With 3-acetylcoumarin both *C*-alkylation and ring-expansion were again observed but the major product was, unexpectedly, the cyclopropane (14a). The stereochemistry of the cyclopropane protons was established by spectroscopic comparisons of chemical shifts with those in the parent compound (15).[10] Models indicate that the initial adduct formed from t-butyldiazomethane and 3-acetyl-coumarin will adopt conformation (16) rather than conformation (17) which contains the equivalent of a 1,3-diaxial interaction between the t-butyl and acetyl groups. On the basis of earlier arguments ring-expansion would again be the favoured process, but now migration of the aryl group may be prevented by collision of the benzene ring with the t-butyl group. We assume



(14) a; R = Ac
b; R = Ph



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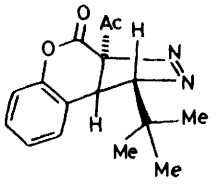

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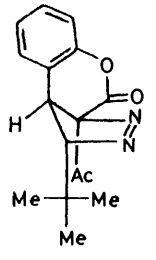

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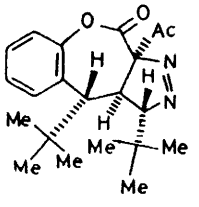

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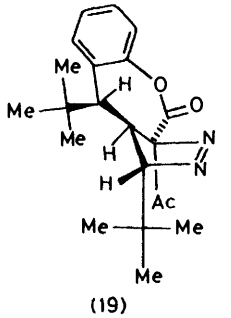
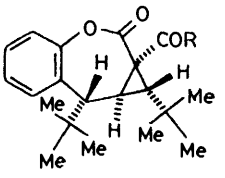


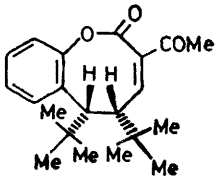
(19)

that, when ring-expansion and *C*-alkylation are both unfavourable processes, cyclopropane formation should predominate.

The 4-neopentylcoumarin (13b) and the oxepino-pyrazoline (18) were isolated in 14% and 12% yield respectively. The ^1H n.m.r. spectrum of the oxepino-pyrazoline confirmed the existence of a proton sequence CH·CH·CH and the torsional coupling constants were consistent with conformation (19) with the C-3a proton pseudo-equatorial. It is interesting to note that the molecule is willing to suffer the equivalent of a 1,3-diaxial interaction in the pyrazoline ring in order to avoid collision of the t-butyl groups. The conformation would normally be that leading to *C*-alkylation, but in either ether or trichloromethane the oxepinopyrazole (18) collapsed to give the cyclopropane (20a) as the



(20) a; R = Me
b; R = Ph



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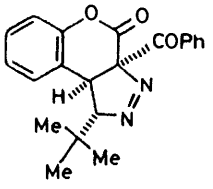

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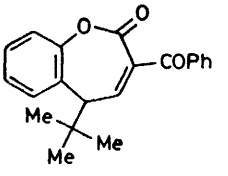


(23)

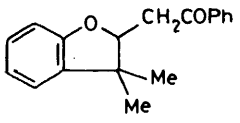
exclusive product. Models indicate that the *C*-alkylation process is blocked by the severe steric congestion that would occur in structure (21).

The ^1H n.m.r. spectrum of the cyclopropane (20a) is complex at 25 °C but simpler at 120 °C indicating that in solution the molecule exists as more than one conformer. The configuration of the cyclopropane was initially assigned on the basis of torsional proton coupling constants, and has been confirmed by *X*-ray crystallography.[3]

With 3-benzoylcoumarin we were able to isolate the initial adduct (22) (55%) despite its marked instability. Also formed during the reaction was the cyclopropane (14b) which was better obtained directly from the adduct (22) (65%). Finally, we were able to isolate a small amount of a substance the p.m.r. spectrum of which was very similar to that of the acetylcyclopropane (20a). The substance is believed to be the benzoyl-cyclopropane (20b), and its isolation indicated that the initial adduct (22) does undergo slight ring-expansion to the oxepin (23) although, as in the diazoethane series,[2] we were unable to isolate this.

We conclude that the bulk of a t-butyl group at C-3 in the pyrazoline ring disfavours both *C*-alkylation and ring-expansion and allows only cyclopropane formation (Scheme). While a moderately bulky diazoalkane is required to initiate ring-expansions, too great a bulk inhibits these and promotes other reactions particularly, inverse additions and cycloproprane formation. Hence ring-expansions are best achieved with diazoethane.

Note on the Use of Silver Nitrate–Alumina.—During the attempted isolation of the oxepin (4b) we found that this changed on silver nitrate–alumina columns, to give the benzofuran derivative (24). No such transformation was observed with either silica or alumina alone, and it appears to involve hydrolysis of the lactone, followed by internal Michael addition of phenolic oxygen to the activated double bond in (25), and decarboxylation.



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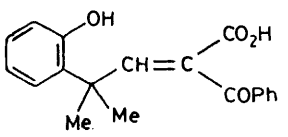

(25)

EXPERIMENTAL

2-Diazopropane was prepared by the mercury(II) oxide oxidation of acetone hydrazone,[11] and t-butyldiazomethane was prepared by the vacuum pyrolysis of the lithium salt of pivalaldehyde tosylhydrazone.[12] Non-hydroxylic solvents were dried over calcium hydride and re-distilled. The light petroleum used was the fraction of b.p. 60—80 °C. U.v. spectra were determined for solutions (*ca.* 10^{-3}M) in ethanol. I.r. spectra (diagnostic bands only) are quoted for KBr discs if no other phase is specified. ^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform, unless otherwise stated, with tetramethylsilane as internal standard; coupling constants (J) are given in Hz. Molecular weights were determined by mass spectrometry.

3-*Cyanocoumarin with* 2-*Diazopropane*.—To a solution of 3-cyanocoumarin (1.0 g) in tetrahydrofuran at 0 °C was added 2-diazopropane (*ca.* 2.0 g) in ether (100 ml) and the mixture maintained at 0 °C. Brisk effervescence began immediately and continued for *ca.* 5 min. After 30 min volatile materials were removed *in vacuo*, without application of heat, leaving a white solid which on crystallisation from acetone–hexane gave 3-*cyano*-4-*isopropylcoumarin* (2a) as pale green needles (1.21 g), m.p. 157—159 °C; $\lambda_{max.}$ 295, 303, and 338 nm (log ε 4.14, 4.13, and 3.87); $\nu_{max.}$ 2 212 (nitrile), and 1 722 cm^{-1} (lactone); τ 2.0—2.8 (4 H, mm; Ar-*H*), 6.26 (1 H, septuplet, *J* 7), and 8.40 (6 H, d, *J* 7) (isopropyl) (Found: C, 73.4; H, 5.4; N, 6.7%; *M*, 213. $C_{13}H_{11}NO_2$ requires C, 73.2; H, 5.2; N, 6.6%; *M*, 213).

3-*Acetylcoumarin with* 2-*Diazopropane*.—To a solution of 3-acetylcoumarin (2.0 g) in ether (100 ml) at 0 °C was added 2-diazopropane (*ca.* 4.0 g) in ether (200 ml) and the mixture maintained at 0 °C for 30 min. Removal of volatile materials *in vacuo*, without application of heat, left a yellow oil which was taken up in ether and the resulting solution filtered. Concentration of the filtrate gave a solid which crystallised from tetrahydrofuran-hexane giving (3aR*, 9bR*)-3a-*acetyl*-3,3a,10,10a-*tetrahydro*-3,3,10,10-*tetramethyl*[1]*benzoxepino*[4,3-c]*pyrazol*-4-*one* (6a) as needles (1.15 g), m.p. 165—166 °C; $\lambda_{max.}$ 232, 265, 273, and 333 nm (log ε 3.55, 2.97, 2.85, and 2.55); $\nu_{max.}$ 1 765 (lactone), 1 685 (ketone), and 1 550 cm^{-1} (N=N); τ 2.5—3.2 (4 H, mm; Ar-*H*), 4.98 (1 H, s; *H*-10a), 7.83 (3 H, s; COMe), 8.00 (6 H, s; 3-Me$_2$), 8.52 (3 H, s), and 9.22 (3 H, s) (10-Me$_2$) (Found: C, 68.2; H, 6.8; N, 9.2%; *M*, 300. $C_{17}H_{20}N_2O_3$ requires C, 68.0; H, 6.7; N, 9.3%; *M*, 300).

3-*Benzoylcoumarin with* 2-*Diazopropane at* 0 °C.—To a solution of 3-benzoylcoumarin (2.5 g) in tetrahydrofuran (50 ml) at 0 °C was added 2-diazopropane (*ca.* 5.0 g) in ether (200 ml) and the mixture maintained at 0 °C for 30 min. Removal of volatile materials *in vacuo*, without application of heat, left a pale yellow oil which on standing under light petroleum–ether (1 : 1 v/v) deposited an intractable white solid which was discarded. On standing the mother liquors deposited a solid which crystallised from benzene–hexane to give (3aR*, 9bR*)-3a-*benzoyl*-3,3a,10,10a-*tetrahydro*-3,3,10,10-*tetramethyl*-4H-[1]*benzoxepino*[4,3-c]*pyrazol*-4-*one* (6b) as prisms (0.21 g), m.p. 145—148 °C; $\nu_{max.}$ (Nujol) 1 725 (lactone), 1 675 (ketone), and 1 558 cm^{-1} (N=N); τ 2.2—2.9 (9 H, mm; Ar-H), 4.50 (1 H, s, H-10a), 7.60 (3 H, s; 3-Me), 7.96 (3 H, s; 3-Me), 8.37 (3 H, s; 10-Me) and 9.26 (3 H, s; 10-Me) (Found: C, 73.1; H, 6.3; N, 7.7%; *M* 362. $C_{22}H_{22}N_2O_3$ requires C, 72.9; H, 6.1; N, 7.7%; *M*, 362).

3-*Benzoylcoumarin with* 2-*Diazopropane at* −10 °C.—To a solution of 3-benzoylcoumarin (4.0 g) in tetrahydrofuran–ether (1 : 1 v/v; 200 ml) was added 2-diazopropane (*ca.* 2.8 g) in ether (40 ml) and the resulting solution maintained at −10 °C. After 3 min glacial acetic acid was added dropwise until the red colour of the diazoalkane was no longer visible. The reaction was then stored at 5 °C for 5 h, during which time marked effervescence was observed. Removal of volatile materials by rotary evaporation left a colourless oil (5.1 g) which was chromatographed over silica gel (600 g) with protection from light. Elution with light petroleum–ether (7 : 3 v/v) gave (1aR*, 7bS*)-1a-*benzoyl*-1,7b-*dihydro*-1,1-*dimethylcyclopropa*[c][1]*benzopyran*-2-(1aH)-*one* (7) as needles (from ethanol) (0.49 g), m.p. 181—182 °C; $\lambda_{max.}$ 252 nm (log ε 4.08); $\nu_{max.}$ 1 730 (lactone) and 1 670 cm^{-1} (ketone); τ 2.0—3.0 (9 H, mm; Ar-*H*), 7.02 (1 H, s; H-7b), 8.82 (3 H, s; Me), and 8.85 (3 H, s; Me) (Found: C, 77.9; H, 5.7%; *M*, 292. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%; *M* 292).

Further elution gave mixtures (0.2 g) which were discarded. Continued elution gave another compound which crystallised from benzene–light petroleum to give 3-*benzoyl*-5,5-*dimethyl*-1-*benzoxepin*-2(5H)-*one* (4b) as prisms (2.18 g), m.p. 138—139 °C; $\lambda_{max.}$ 252 (log ε 4.04); $\nu_{max.}$ 1 720 (lactone) and 1 660 cm^{-1} (ketone); τ 2.3—2.8 (9 H, mm; Ar-*H*), 2.66 (1 H, s; H-4), and 8.34 (6 H, s; CMe$_2$) (Found: C, 77.9; H, 5.5%; *M*, 2.92. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%; *M*, 292).

Further elution gave 3-*benzoyl*-4-*isopropylcoumarin* (2b) as needles (from benzene) (0.95 g), m.p. 198°, $\lambda_{max.}$ 254, 280, and 310 nm (log ε 4.03, 4.00, and 3.79); $\nu_{max.}$ 1 706 (lactone) and 1 663 cm^{-1} (ketone); τ 2.0—2.8 (9 H, mm; Ar-*H*), 6.80 (1 H, septuplet; *J* 7), and 8.63 (6 H, d, *J* 7; CH*Me*$_2$). (Found: C, 78.2; H, 5.6%; *M*, 282. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%; *M*, 292).

Benzoxepin (4b) *with Silver Nitrate-Alumina*.—The benzoxepin (4b) (0.29 g) was adsorbed into a 28% silver nitrate-alumina column (10 g) which was stored for 3 days in the dark. Elution with light petroleum–ether (4 : 1 v/v) gave a solid which was recrystallised from ether–hexane to give 2,3-*dihydro*-3,3-*dimethyl*-2-*phenacylbenzofuran* (24) as prisms (0.142 g), m.p. 71—72 °C; $\lambda_{max.}$ 247 and 277 nm (log ε 4.00 and 3.70); $\nu_{max.}$ 1 686 cm^{-1} (ketone); τ 2.0—2.93 (9 H, mm, Ar-*H*), 5.02, 6.46 and 6.47 (3 H; ABX system; J_{AB} 16.5 Hz, J_{AX} 8.2 Hz and J_{BX} 4.8 Hz; OC*H*·C*H*$_2$), 8.58 (3 H, s; Me), and 8.77 (3 H, s; Me) (Found: C, 81.1; H, 6.7%; *M*, 266. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%; *M*, 266).

Benzoxepin (4b) *with Diazoethane*.—To a solution of the benzoxepin (4b) (0.5 g) in tetrahydrofuran (15 ml) at 0 °C was added diazoethane (*ca.* 0.50 g) in ether (100 ml) and the mixture maintained at 0 °C for 30 min. Removal of volatile materials *in vacuo*, without application of heat, gave an oil which on standing under hexane gave (1R*,3aR*,10aR*)-3a-*benzoyl*-1,3a,10,10a-*tetrahydro*-1,10,10-*trimethyl*[1]*benzoxepino*[3,4-c]*pyrazol*-4-*one* (10) as prisms (0.59 g), m.p. 122—124 °C (with loss of nitrogen); $\nu_{max.}$ 1 750 (lactone), 1 682 (ketone) and 1 545 cm^{-1}; τ 1.8—2.0 (9 H, mm; Ar-*H*), 5.45 (1 H, dq, *J* 10 and 7; H-3), 6.83 (1 H, d, *J*, 10; H-3a), 8.20 (3 H, d, *J* 7; 3-Me), 8.40 (3 H, s; 4-Me), and 8.60 (3 H, s; 4-Me) (Found: C, 72.5; H, 6.0; N, 8.1%. $C_{21}H_{20}O_3N_2$ requires C, 72.4; H, 5.8; N, 8.0%).

Thermolysis of the Benzoxepinopyrazole (10).—A solution of the benzoxepinopyrazole (0.59 g) in dry benzene (50 ml) was refluxed for 6 h under anhydrous conditions. Removal of the solvent by rotary evaporation left an oil which crystallised from hexane–benzene to give 3-*benzoyl*-4-*ethyl*-5,5-*dimethyl*-1-*benzoxepin*-2(5H)-*one* (11) as prisms (0.34 g), m.p. 165—167 °C; $\lambda_{max.}$ 245, 255 (infl.), and 283 nm (log ε 4.07, 3.99, and 3.80); $\nu_{max.}$ 1 690 (lactone) and 1 665 cm^{-1} (ketone); τ 2.3—3.0 (9 H, mm; Ar-*H*), 7.77 (2 H, q, *J*-7; C*H*$_2$Me), 8.28 (6 H, s: Me$_2$), and 9.00 (3 H, t, *J*-7; CH$_2$*Me*) (Found: C, 78.9; H, 6.3%; *M*, 320. $C_{21}H_{20}O_3$ requires C, 78.7; H, 6.3%; *M*, 320).

The mother-liquors were separated by preparative t.l.c. on silica using benzene as eluant. Extraction of the major band with chloroform gave an oil, which crystallised from hexane to give (1R*,1aS*,8aR*)-1a-*benzoyl*-1,1a,8,8a-*tetrahydro*-1,8,8-*trimethyl*-2H-*cyclopropa*[c][1]*benzoxepin*-2-*one* (12) as prisms, m.p. 116—117 °C; $\lambda_{max.}$ 247 nm (log ε 4.18); $\nu_{max.}$ 1 700 (lactone) and 1 680 cm^{-1} (ketone); τ 2.0—3.1 (9 H, mm; Ar-*H*), 7.8 (2 H, AB system; H-8 and H-8a), 8.32 (6 H, s; CMe$_2$), and 9.11 (3 H, d; *J* 6; 8-Me) (Found: C, 78.7; H, 6.3%; *M*, 320. $C_{21}H_{20}O_3$ requires C, 78.7; H, 6.3%; *M*, 320).

3-*Cyanocoumarin with t-Butyldiazomethane*.—To a solution of 3-cyanocoumarin (0.30 g) in tetrahydrofuran (20 ml) was added t-butyldiazomethane (*ca.* 0.50 g) in ether (100 ml). The solution was left overnight in the dark at room temperature. Removal of volatile materials *in vacuo*, without application of heat, left a solid which on recrystallisation from acetone–light petroleum gave 3-*cyano*-4-(2,2-*dimethylpropyl*)*coumarin* (13a) as prisms (0.33 g), m.p. 163—165 °C; $\lambda_{max.}$ 297, 304, and 340 nm (log ε 4.12, 4.11, and 3.86); $\nu_{max.}$ 2 212 (CN) and 1 728 cm^{-1} (lactone); τ 2.1—2.8 (4 H, m, Ar-*H*), 6.90 (2 H, s; CH$_2$), 8.74 (3 H, s; Me), and 8.88 (6 H, s; Me$_2$) (Found: C, 74.5; H, 6.3; N, 5.8%; M, 241. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%; *M*, 241).

3-*Acetylcoumarin with t-Butyldiazomethane*.—To a solution of 3-acetylcoumarin (0.50 g) in tetrahydrofuran (10 ml) was added t-butyldiazomethane (*ca.* 1.0 g) in ether (100 ml) and the resulting solution maintained at 0 °C for 4 h. Removal of volatile materials *in vacuo*, without application of heat, left an oil which on standing under light petroleum yielded (1R*,3aS*,10S*,10aS*)-3a-*acetyl*-1,10-*di*-*t*-*butyl*-1,3a,10,10a-*tetrahydro*-4H-[1]*benzoxepino*-[3,4-c]-*pyrazol*-4-*one* (18) as prisms (0.13 g), m.p. 124 °C (decomp.); $\nu_{max.}$ 1 720 (broad; lactone and ketone) and 1 555 cm^{-1} (N=N); τ 2.6—3.1 (4 H, mm; Ar-*H*), 5.70 (1 H, d, *J* = 4; H-3), 6.58 (1 H, dd, *J* 4 and 2.5; H-3a), 7.55 (3 H, s; COMe), 7.63 (1 H, d, *J* 2.5; H-4), 8.90 (9 H, s; t-butyl), and 9.04 (9 H, s; t-butyl) (Found: C, 70.8; H, 8.1; N, 7.9%. $C_{21}H_{28}N_2O_3$ requires C, 70.8; H, 7.9; N, 7.9%).

Evaporation of the mother-liquors gave a crystalline mass contaminated with an oil. Recrystallisation from pentane gave (1R*,1aR*,7bR*)-1a-*acetyl*-1-*t*-*butyl*-1a,7b-*dihydrocyclopropa*[c][1]*benzopyran*-2(1H)-*one* (14a) as prisms (0.42 g), m.p. 105 °C; $\lambda_{max.}$ 226, 269, and 276 nm (log ε 3.45, 2.96, and 2.92); $\nu_{max.}$ (Nujol) 1 723 (lactone) and 1 700 cm^{-1} (ketone); τ 2.4—3.1 (4 H, mm; Ar-*H*), 6.70 (1 H, d, *J* 7.5; H-7b), 7.29 (3 H, s; COMe), 8.34 (1 H, d, *J* 7.5; H-1), and 9.00 s, t-butyl) (Found: C, 74.2; H, 7.1%; *M*, 258. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%; *M*, 258).

The residue was separated by preparative t.l.c. on silica gel using the solvent system light petroleum–ether (1 : 1 v/v). Extraction of the major band gave an oil which crystallised from hexane to give 3-*acetyl*-4-(2,2-*dimethylpropyl*)*coumarin* (13b) as prisms (0.1 g), m.p. 112—114 °C; $\lambda_{max.}$ 290 and 320 (infl.) nm (log ε 3.93 and 3.76); τ 2.1—2.9 (4 H, mm; Ar-*H*), 6.94 (2 H, s; C*H*$_2$), 7.41 (3 H, s; COMe), 8.98 (3 H, s; Me), and 9.02 (6 H, s; CMe$_2$) (Found: C, 74.6; H, 7.0%; *M*, 258. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%; *M*, 258).

Decomposition of the Oxepinopyrazole (18).—A solution of the oxepinopyrazole (0.10 g) in dry chloroform was left at room temperature for 24 h, during which time steady nitrogen evolution was observed. Removal of the solvent left an oil which on standing under hexane deposited (1R*,1aS*,8R*,8aS*)1a-*acetyl*-1,8-*di*-*t*-*butyl*-1,1a,8,8a-*tetrahydrocyclopropa*[c][1]*benzoxepin*-2-*one* (20a) as prisms (0.082 g), m.p. 119 °C; $\lambda_{max.}$ 265 and 272 nm (log ε 2.82 and 2.13); $\nu_{max.}$ ($CHCl_3$) 1 740 (lactone) and 1 700 cm^{-1} (ketone); τ($CHCl_2CHCl_2$; 120 °C) 7.28 (2 H, m, *J* 4.5 and 4.5; H-1 and H-8), 7.61 (3 H, s; COMe), 7.90 (t, 1 H; *J* 4.5; H-8a), 8.66 (9 H, s; t-butyl), and 8.95 (9 H, s; t-butyl) (Found: C, 77.0; H, 8.8%; *M*, 328. $C_{22}H_{28}O_3$ requires C, 76.8; H, 8.6%; *M*, 328).

3-*Benzoylcoumarin with t-Butyldiazomethane*.—To a solution of t-butyldiazomethane (*ca.* 1.0 g) in ether at 0 °C was added 3-benzoylcoumarin (0.50 g) in tetrahydrofuran (10 ml) and the resulting solution maintained at 0 °C for 4 h. Concentration of the solution, without application of heat, resulted in the separation of (1R*,3aR*,9bR*)-3a-*benzoyl*-1-*t*-*butyl*-3a,9b-*dihydro*[1]*benzopyrano*[3,4-c]*pyrazol*-4(1H)-*one* (22) as a powder (0.39 g), which was satisfactorily pure after washing with cold hexane. For analytical purposes the compound was slowly precipitated from cold tetrahydrofuran with hexane, which gave needles, m.p. 87 °C (with loss of nitrogen); $\nu_{max.}$ 1 750 (lactone), 1 690 (ketone) and 1 555 cm^{-1} (N=N) (Found: C, 72.5; H, 5.8; N, 7.9%. $C_{21}H_{20}N_2O_3$ requires C, 72.4; H, 5.8%; N, 8.0%).

Concentration of the mother-liquor gave an oil which on standing under ethane–hexane yielded (1R*,1aR*,7bR*)-1a-*benzoyl*-1-*t*-*butyl*-1a,7b-*dihydrocyclopropa*[c]-[1]*benzopyran*-2(1H)-*one* (14b) as prisms (0.21 g), m.p. 176—177 °C; $\lambda_{max.}$ 250 nm (log ε 4.17); $\nu_{max.}$ 1 744 (lactone) and 1 658 cm^{-1} (ketone); τ 1.9—3.0 (9 H, mm; Ar-*H*), 7.06 (1 H, d, *J* 7; H-7b), 8.28 (1 H, d, *J* 7; H-1), and 9.00 (9 H, s; t-butyl) (Found: C, 78.4; H, 6.3%; *M*, 320. $C_{21}H_{20}O_3$ requires C, 78.7; H, 6.3%; *M*, 320).

Preparative t.l.c. on silica (benzene eluant) of the residue supplied a solid which on recrystallisation from hexane gave (1R*,1aS*,8R*,8aS*)-1a-*benzoyl*-1,8-*di*-*t*-*butyl*-1,1a,-8,8a-*tetrahydrocyclopropa*[c][1]*benzoxepin*-2-*one* (20b) as

prisms, m.p. 156—158 °C; $\lambda_{max.}$ 250 nm (log ε 4.20); $\nu_{max.}$ 1 715 (lactone) and 1 670 cm^{-1} (ketone); τ 1.9—2.5 (9 H, mm; Ar-*H*), 6.8—8.0 (3 H, mm; H-1, H-8 and H-8a), 8.74 and 8.90 (9 H, two singlets; t-butyl) and 9.00 and 9.36 (9 H; two singlets, t-butyl) (Found: $M^{+\bullet}$, 390.215 88. $C_{26}H_{30}O_3$ requires *M*, 390.219 48.

Decomposition of Chromenopyrazole (22).—A solution of the chromenopyrazole (0.174 g) in ether (5 ml) was stored in the dark at 20 °C for 48 h. Removal of the solvent under reduced pressure left a white solid (0.161 g) which on recrystallisation from benzene–hexane gave cyclopropabenzopyran (14b) as prisms (0.108 g; 68%), m.p. 176—177 °C. An identical result was obtained when the reaction was carried out in trichloromethane.

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