On Stevens' Tropolone Synthesis; Hydrolysis of Spirocyclopentadiene– and Spiroindene–Dichloroketen Adducts

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Hydrolysis of the spiro[2.4]hepta-4,6-diene–dichloroketen adduct (2a) gave 3-(2'-acetoxyethyl)-1*H*-cycloheptatrien-1-one (3a) and dihydro-8*H*-cyclohepta[*b*]furan-8-one (4a), of which the former was the precursor to the latter. 1-Methylspiro[2.4]hepta-4,6-diene– and spiro(cyclopropane-1,1'-[1*H*]-indene)–dichloroketen adducts, (2b), (2c), and (6), gave similar results.

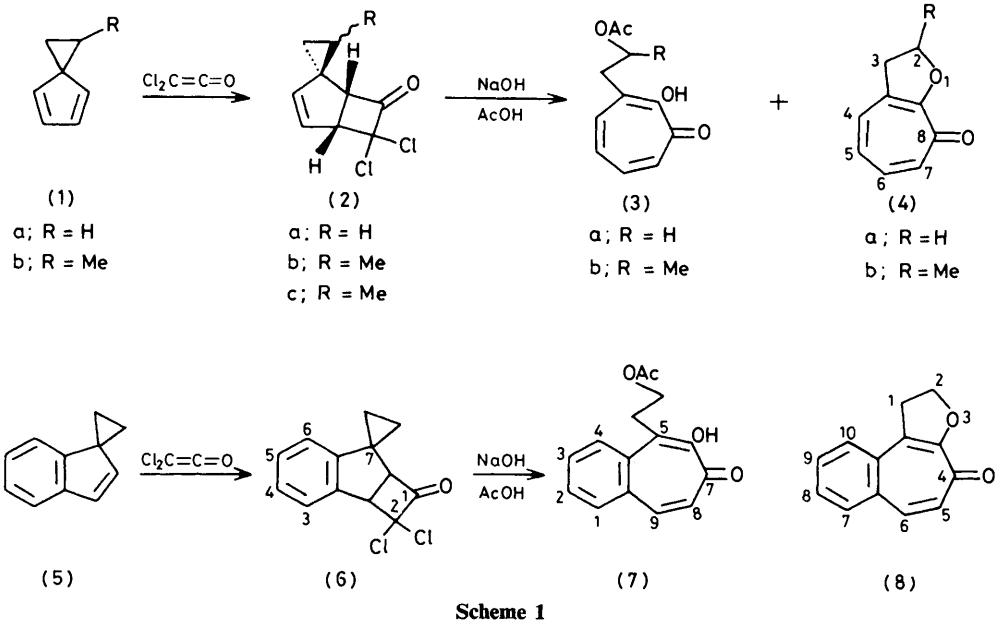
The spiro[4.4]nona-1,3-diene–dichloroketen adduct (10) gave spiro[4,6]undeca-8,10-diene-6,7-dione (14), 6-hydroxy-1,2,3,4-tetrahydro-5*H*-benzocyclohepten-5-one (15) and -7*H*-benzocyclohepten-7-one (16), and 5-acetoxy- and 5-hydroxy-7-chlorospiro(bicyclo[3.2.0]hept-2-ene-4,1'-cyclopentane)-6-ones, (12) and (13). The spiro(cyclopentane-1,1'-[1*H*]-indene)–dichloroketen adduct (19) gave similarly spiro(5*H*-benzocycloheptene-5,1'-cyclopentane)-6,7-dione (22).

The formation of these compounds, especially the seven-membered ring, can be explained by the application of Bartlett's mechanism to Stevens' tropolone synthesis.

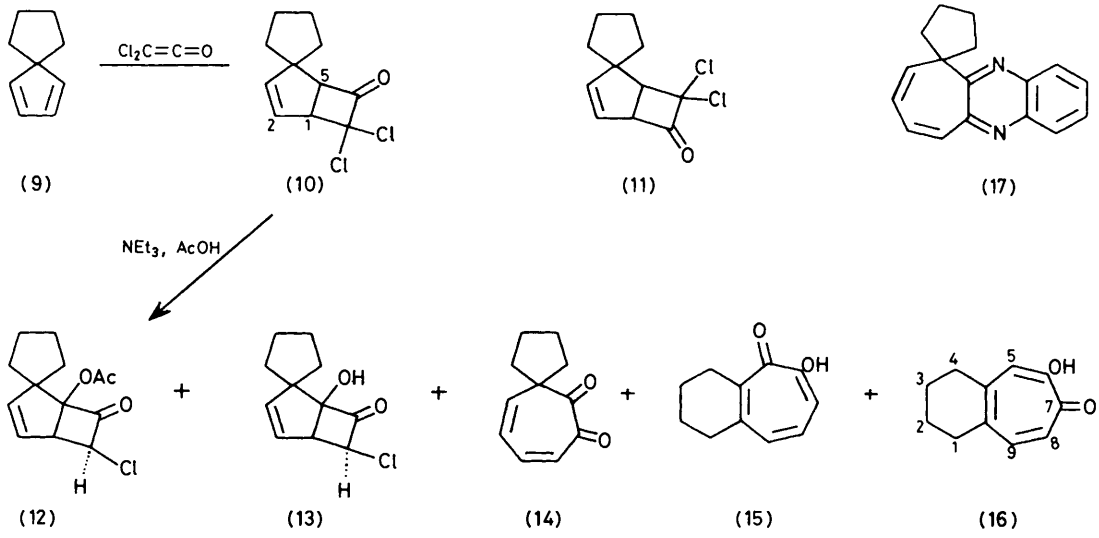
Among many methods for the synthesis of tropolones,[1] the synthesis published by Stevens in 1965,[2] involving the hydrolysis of $[_{\pi}2_s + _{\pi}2_a]$ cyclopentadiene–dichloroketen adducts,[3] seems to be most widely used today, although a drawback of this method is that it is not possible to introduce a substituent in the 5-position of the tropolone ring because it is difficult to introduce a substituent uniquely into the 2-position of cyclopentadiene. The method has been successfully applied to the total synthesis of natural products such as α-dolabrin,[4] thujaplicin,[5] and colchicine,[6] and the synthesis of non-benzenoid quinones such as heptalene-1,8- and -3,8-dione derivatives,[7] and pleiadiene-7,8-dione.[8]

In the present paper we describe the synthesis of some new troponoid compounds by the hydrolysis of spirocyclopentadiene–dichloroketen adducts (an extension of Stevens' method) and briefly discuss the mechanism of their formation.

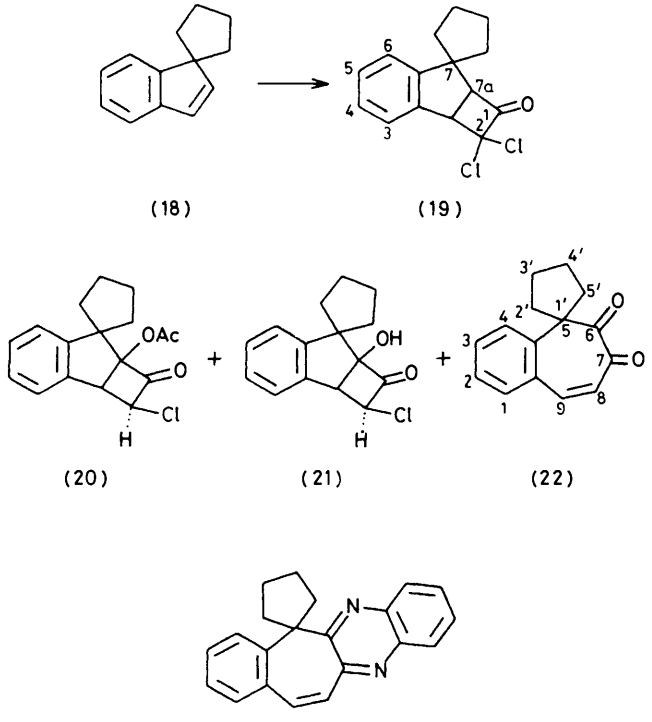
The spiro[2.4]hepta-4,6-diene–dichloroketen adduct (2a)[9] was hydrolysed with sodium acetate in refluxing acetic acid to afford the acetoxyethyltropolone (3a) (1.6% yield) and the cycloheptafuranone (4a) (33% yield). The tropolone (3a) gave a red colour with iron(III) chloride and gave a green copper salt with copper(II) acetate. Compound (4a) showed aliphatic ^{1}H n.m.r. (200 MHz) absorptions as two triplets [δ 3.45 (2 H) 4.72 (2 H)] and four aromatic protons as multiplets. Its ^{13}C n.m.r. spectrum showed the presence of three quaternary, four tertiary, and two secondary carbon atoms. Its i.r. spectrum showed two characteristic tropone bands[10] at 1 619 and 1 562 cm^{-1} due to C=C and C=O stretching vibrations. Compound (3a) was hydrolysed to give (4a) in 43.7% yield, showing that it was the precursor of (4a). The reaction of 1-methylspiro[2.4]hepta-4,6-diene (1b) with dichloroketen led to a mixture of two adducts (2b) and (2c) (92.5% yield), in a ratio of 11 : 9 (n.m.r.). The position and configuration of the methyl group were not determined but consideration of molecular models indicated that compounds (2b) and (2c) were isomeric at position 8 as depicted. The mixture of (2b)



Scheme 1



Scheme 2



Scheme 3

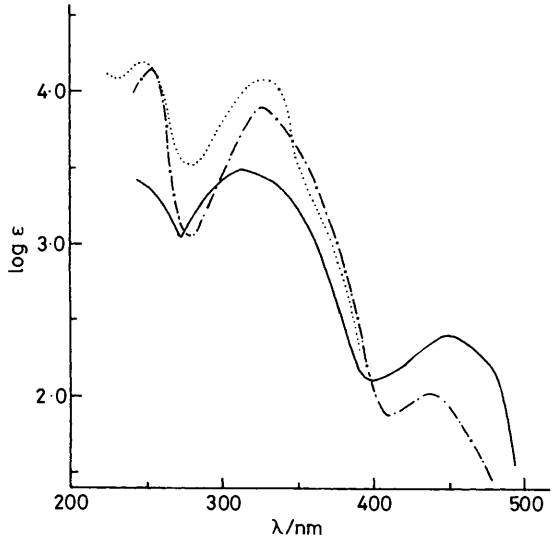
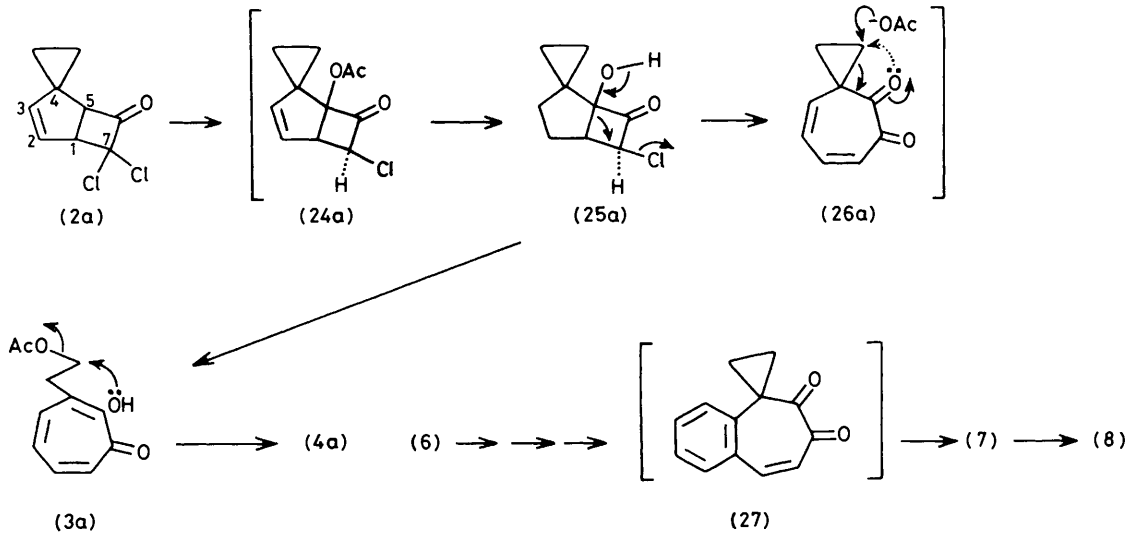


Figure. Electronic spectra of α-diketones: ——— spiro-diketone (14) (solution in chloroform); — · — · — benzospirodiketone (22) (solution in chloroform); ..... 3-bromo-4,5-benzo-4,6-cycloheptadiene-1,2-dione [16] (solution in methanol).

and (2c) was hydrolysed as for (2a) to give the acetoxypropyltropolone (3b) (12.8% yield) and the methylcycloheptafuranone (4b) (26.7% yield). Hydrolysis of compound (3b) gave (4b), showing that it was a precursor of (4b). Hydrolysis of the spiro-compound (6),[11] a benzo-fused analogue of (2a) with sodium acetate in refluxing acetic acid as for compounds (2))afforded the benzo-fused tropolone (7) (8% yield) and the benzocycloheptafuranone (8) (68% yield). Under similar conditions of hydrolysis, the acetate (7) was transformed into compound (8) in 82% yield, again showing that (7) was the precursor of (8).

The addition of dichloroketen to spiro[4.4]nona-1,3-diene (9) [12] yielded 55.4% of a single dichlorocyclobutanone ($\nu_{C=O}$ 1 806 cm^{-1}), either (10) or (11), which g.l.c. and n.m.r. analyses showed to be at least 97% pure. Structure (10), the 7-oxo-compound, was readily assigned to this adduct by analogy with the adduct (2a).* The adduct (10) was hydrolysed with a mixture of aqueous acetic acid and triethylamine at room temperature for 43 h to yield five products: the 5-acetoxy-7-*exo*-chloroketone (12) (16% yield) ($\nu_{C=O}$ 1 804 and 1 734 cm^{-1}), the corresponding hydroxy-ketone (13) (25% yield) ($\nu_{C=O}$ 1 794 cm^{-1}, ν_{OH} 3 570 cm^{-1}), spiro[4.6]undecadienedione (14) (8% yield), tropolone (15) (1.5% yield) and tropolone (16) (5.1% yield). The 1-H n.m.r. signals for (12) (δ 4.00, dd, *J*. 9.0 and 2.5 Hz) or (13) (δ 3.18 dd, *J* 7.0 and 1.9 Hz) can be

* If it is assumed that the cycloaddition is not completely concerted and some charge develops in the transition state, the partially charged species leading to bicyclo[3.2.0]hept-2-en-6-ones are stabilised by allylic resonance [9,19]



Scheme 4

interpreted only on the basis that the addition of dichloroketen gave a 6- rather than a 7-oxo-adduct. The 7-H of (12) or (13) was not coupled with 1-H, showing that the dihedral angle between them was almost 90°. The structure of the spiro-diketone (14) was evidenced by the i.r. ($\nu_{C=O}$ 1 716 and 1 656 cm^{-1}), u.v., ^1H n.m.r., and ^{13}C n.m.r. (three quaternary, four tertiary, and four secondary carbons) spectral data, and its formation of the quinoxaline derivative (17) (62.4% yield) on reaction with *o*-phenylenediamine. The physical properties of the tropolone (16) corresponded well with those reported for the substance prepared by a different procedure.[14] The structure of the tropolone (15) was easily assigned by comparing the spectral data with those of the isomer (16). This hydrolysis was repeated under different conditions some twenty times; a maximum yield of the spiro-diketone (14) of 65% was obtained at one time and a 45% yield of a mixture of tropolones (15) and (16) was obtained at another; optimum conditions were not, however, established. The hydroxy-ketone (13) was hydrolysed similarly to give (14), (15), and (16), thus showing it was a precursor to these compounds.

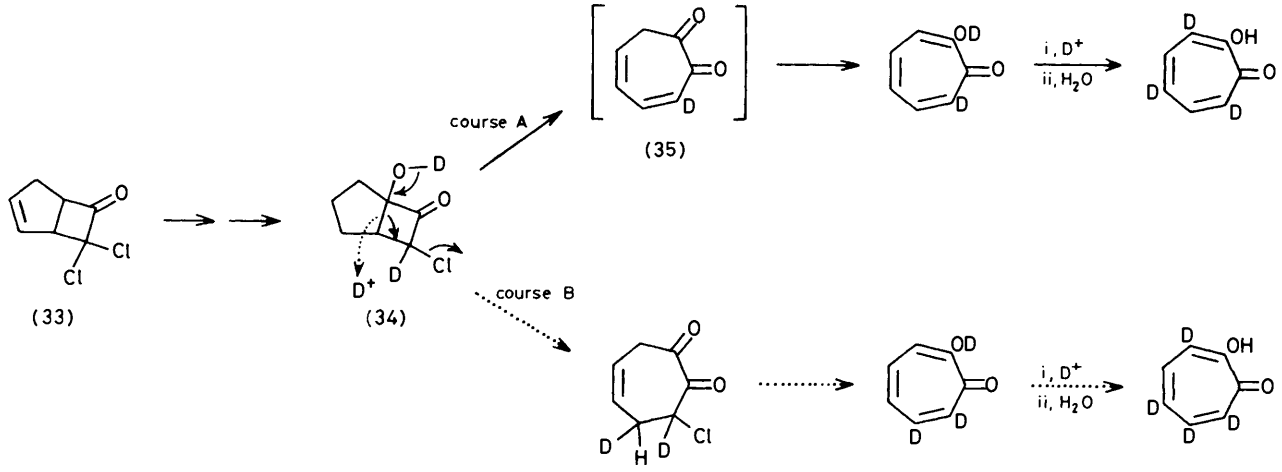
Dichloroketen was allowed to react with spiro(cyclopentane-1,1′-[1*H*]-indene) (18)[15] to afford a 58% yield of a single dichlorocyclobutanone ($\nu_{C=O}$ 1 804 cm^{-1}), to which structure (19) was assigned; the assignment was based on arguments similar to those used above for the structural assignment of (10). Hydrolysis of (19) afforded the acetate (20) ($\nu_{C=O}$ 1 792 and 1 730 cm^{-1}), the hydroxy-ketone (21) ($\nu_{C=O}$ 1 770 cm^{-1}, ν_{OH} 3 300 cm^{-1}), and spiro(benzocycloheptene-5,1′-cyclopentane)dione (22) (45% yield, $\nu_{C=O}$ 1 719 and 1 663 cm^{-1}), which yielded the quinoxaline derivative (23) (97% yield) on treatment with *o*-phenylenediamine to confirm the assigned α-diketone structure. Electronic spectra of (14) and (22) are presented in the Figure in comparison with that of 3-bromo-4,5-benzocycloheptadiene-1,2-dione.[16] For (14) and (22) homoquinone character may be expected, but little tendency such as this was recognized by the comparison of their spectroscopic data with those[17] for *o*-benzoquinone and *o*-naphthoquinone respectively.

The reaction sequence of the formation of (3a), (4a), (7), and (8) can be considered as shown in Scheme 4. The formation of the seven-membered ring can be explained in terms of Bartlett's mechanism[18] but not Kitahara's;[4,19] for the conversion of (6) into (7) and (8), the only possible intermediate would be the spiro-diketone (27). Assuming, first, formation of the seven-membered ring,* the cyclopropane ring must be cleaved to give the spiro-diketone (26a), which may be regarded as a kind of cyclopropyl ketone. The cyclopropyl ring of (26a) or (27) would then be cleaved by attack of an acetate ion together with aromatization of the seven-membered ring to form the acetate (3a) or (7). Besides the transformation of these acetates into dihydrofurotropones, however, a mechanism involving a concerted cyclopropane ring opening with neighbouring group participation by carbonyl oxygen and aromatization of the seven-membered ring of (26a) or (27) to form the dihydrofuran (4a) or (8) cannot be completely ruled out.† The possible mechanism of the formation of (12), (13), (14), (15), and (16) is shown in Scheme 6.‡ Dechlorin-

* This would be reasonable unless a norcaradienone intermediate[4,19,20] were involved.

† Cyclopropanecarbaldehyde is known to rearrange to dihydrofuran at 375 °C[21] but acetylcyclopropane does not.[22] Acid hydrolysis of cyclopropyl ketone is known to give γ-hydroxy ketone[23] or tetrahydrofuran[24] but no dihydrofuran. Some enones are known to give dihydrofurans by *in situ* reactions with difluorocarbene[25] or methylene ylide[26] but no evidence of the intermediary formation of cyclopropyl ketone was given in those papers and other explanation would be possible as was pointed by those authors.

‡ Although a concerted process from the hydroxy-ketone to tropolone had been proposed,[18] we examined if the reaction really proceeded stepwise or concertedly. On solvolysis of α-dichloroketone (33) in deuterium media, if it proceeded concertedly (Course A), the incorporation of deuterium would be three, while if it proceeded stepwise (course B), four deuteriums would be incorporated (Scheme 5); S. Itô, J. Tsunetsugu, T. Kanno, H. Sugiyama, and H. Takeshita, *Tetrahedron Lett.*, 1965, 3659. The result of solvolysis experiments in deuterium media are shown in Table 1. Runs (A) and (B) showed three incorporated deuteriums and no significant difference between them, eliminating a two-step mechanism (Course B) and supporting the concerted mechanism (Course A). In order to obtain Bartlett's imaginary diketone (35),[18] dichloro-ketone (33) was hydrolysed in the presence of *o*-phenylenediamine under different conditions but no quinoxaline-type compound was obtained.



Scheme 5

Table. Number and ratio (%) of incorporated deuterium atoms into tropolone on solvolysis of dichloroketen–cyclopentadiene adduct (33) in deuterium media

	Number of deuterium atoms				
Conditions	0	1	2	3	4
(A)	2.63	13.00	41.46	42.91	0.0
(B)	6.67	16.24	40.34	36.75	0.0
(C)	92.46	1.39	3.28	2.87	0.0

Conditions (A); solvolysis of the adduct (33) with refluxing in a mixture of AcONa and AcOD and acidification with 10% HCl. Conditions (B); refluxing a mixture of tropolone, AcONa, and AcOD and acidification with 10% HCl. Conditions (C); refluxing a mixture of tropolone, AcONa, and AcOH and acidification with 10% DCl and washing with water. Number of incorporated deuterium atoms was determined by mass spectroscopy (S. Itô, J Tsunetsugu, T. Kanno, H. Sugiyama, and H. Takeshita *Tetrahedron Lett.*, 1965, 3659).[3]

ation of (10) would generate a cation,* which on attack by acetate ion would form the acetate (12); this would then be hydrolysed to form the α-hydroxy-ketone (13). Compound (13) would be transformed into the spiro-diketone (14) which on rearrangement, either by 1,7-addition of acetic acid or by protonation of the carbonyl oxygen, would form a bicyclic intermediate, either (28) or (29), both of which would lead to the tropolone (15) by elimination of either acetic acid or a proton. On the other hand, (13) would rearrange to the α-keto-alcohol (30) by fission of the C(4)–C(5) bond with electron input and withdrawal respectively from the hydroxy and carbonyl groups. Rearrangement of (30) would then give the diketone (31) by the elimination of a chlorine atom as a result of electron input from the hydroxy-group. The addition of acetic acid and migration of a cyclopentane ring would form a bicyclic compound (32), which by the elimination of acetic acid and aromatization would become the tropolone (16).†

Experimental

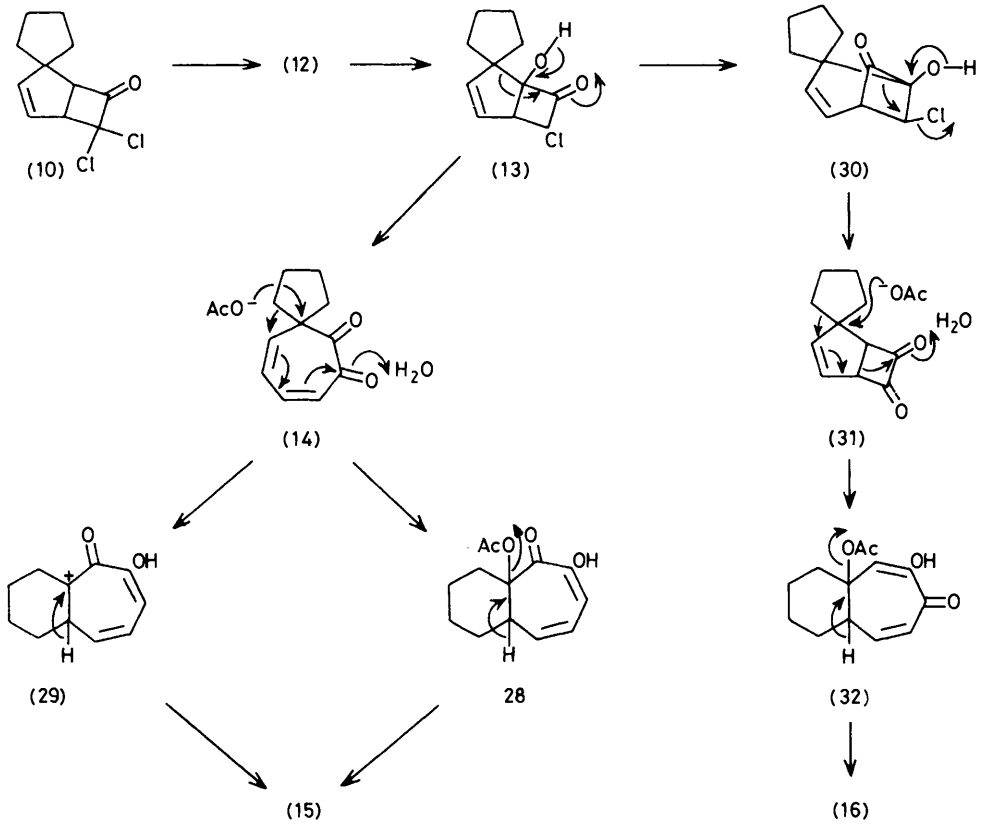
M.p.s were determined with a Mitamura air-bath apparatus and are uncorrected. ^{1}H n.m.r. spectra (internal $SiMe_4$) were determined with a Varian A-60 D spectrometer. I.r. spectra were determined with a JASCO A-2, electronic spectra (u.v.) with a Hitachi 340, and mass spectra with a JEOL-JMS-01SG-2 spectrometers. The spectral parameters refer to the following condition unless otherwise stated: u.v., $CHCl_3$; i.r., $CHCl_3$; ^{1}H n.m.r., $CDCl_3$. Preparative column chromatography was done with using Kieselgel 60 (Merck 70—230 mesh).

General Procedure for Addition of Dichloroketen to Spirocyclopentadienes and Spiroindenes.—Dichloroacetyl chloride was added dropwise during *ca.* 3—5 min to a rapidly stirred mixture of 1 equiv. of triethylamine in a 3- to 5-fold excess of the spirocyclopentadiene and an equal volume of dry hexane. After a further 5 min the mixture was poured into water and the organic phase was washed with 2M sodium carbonate, 2M-hydrochloric acid, and water, and dried over anhydrous magnesium sulphate. After removal of the solvent and excess of spirocyclopentadiene, the crude product was purified by silica-gel chromatography with methylene dichloride as an eluant and distilled under reduced pressure. Spiroindenes were treated in a similar way to the above except that a reaction mixture was refluxed for 24 h after addition of dichloroacetyl chloride.

(a) 7,7-*Dichlorospiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1′-*cyclopropan*)-6-*one* (2a). Dichloroacetyl chloride (3.47 g, 23.6 mmol) was allowed to react with spiro[2.4]hepta-4,6-diene (1a) in the above way to give the tricyclic dichloro-ketone (2a) (2.64 g, 55.1%) as a liquid, b.p. 71—72 °C at 5.5 mmHg, which showed practically the same n.m.r. and i.r. spectral characteristics as those reported earlier:[9] $\nu_{max.}$ (neat) 1 801

* In Bartlett's mechanism,[18] a bridgehead and enol allylic cation,[27] or 1,3-dipolar species [28] seemed to be assumed for the bicyclo-[3.2.0]hept-2-en-6-one system by analogy with the cyclobutane system. A referee has pointed out the uncertain existence of this kind of species and certainly it was difficult for us to find the clear evidence in the literature [29] for it. In our experiments and others quoted in this paper, however, positive evidence for the intermediary existence of a non-classical ion such as monohomocyclopropyl cation [30] was not obtained, although no kinetic study on this reaction has been recorded yet. See also: W. T. Brady and J. P. Hiekle, *J. Am. Chem. Soc.*, 1972, **94**, 4278; G. L. Buchanan, *Chem. Soc. Rev.*, 1974, **3**, 41; K. E. Heine and R. F. Childs, *Can. J. Chem.*, 1976, **54**. 12; B. Szechner and A. S. Dreiding, *Helv. Chim. Acta*, 1976, **59**, 21; G. Jones II and L. P. McDnell, *J. Am. Chem. Soc.*, 1976, **98**, 6023; A. Greenberg and J. F. Liebman, 'Strained Organic Molecules,' Academic Press, London, 1978, p. 133.

† From our results, however, it is clear that Bartlett's mechanism is a general working principle for formation of a seven-membered skeleton from 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-ones.



Scheme 6

cm^{-1} (C=O); δ 0.58—1.43 (4 H, m, cyclopropyl), 3.74 (1 H, d, *J* 7.2 Hz), 4.26 (1 H, d, *J* 7.8 Hz), 5.58 (1 H, dd, 1.8 and 5.4 Hz, 3-H), and 5.77 (1 H, dd, *J* 2.4 and 5.4 Hz, 2-H).

(b) 7,7-*Dichloro-2'methylspiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1'-*cyclopropan*)-6-*one* (2b) *and* (2c). Dichloroacetyl chloride (22.4 g, 154 mmol) was allowed to react with 1-methylspiro-[2.4]hepta-4,6-diene (1b) similarly to give a mixture of the tricyclic dichloro-ketones (2b) and (2c) (25.79 g, 92.5%) as a yellow oil, b.p. 106—108 °C at 7 mmHg (Found: C, 55.5; H, 4.7. $C_{10}H_{10}Cl_2O$ requires C, 55.32; H, 4.60%), $\nu_{max.}$ (neat) 1 793br cm^{-1} (C=O); δ 0.33—1.80 (6 H, m, methyl, cyclopropyl), 7.22 (0.55 H, d, *J* 7.6 Hz, 5-H), 7.79 (0.45 H, d, 7.3 Hz, 5-H), 8.44 (2 H, d, *J* 7.6 and 7.3 Hz, 1-H), 5.46—5.77 (1 H, m, olefinic, 2-H), and 5.77 (1 H, m, olefinic, 3-H).

(c) 2,2-*Dichloro-2a,7a-dihydrospiro*-(7H-*cyclobut*[a]*indene*-7,1'-*cyclopropan*]-1(2H)-*one* (6). Dichloroacetyl chloride (7.15 g, 48.5 mmol) was allowed to react with spiro(cyclopropane-1,1'-[1*H*]-indene) (5) [11] to give the dichloro-ketone (6) (6.53 g, 53.4%) as a liquid, b.p. 143—145 °C at 4 mmHg, m.p. 96—97 °C (colourless needles from hexane) (Found: C, 61.7; H, 3.85. $C_{13}H_{10}Cl_2O$ requires C, 61.42; H, 4.05%), $\nu_{max.}$ (KBr) 1 795 cm^{-1} (C=O); δ 0.60—1.82 (4 H, m, cyclopropyl), 3.99 (1 H, d, *J* 8.2 Hz), 4.63 (1 H, d, *J* 8.2 Hz), 6.60—6.82 (1 H, m, aromatic), 7.20—7.55 (3 H, m, aromatic). The compound gave one spot by t.l.c.

(d) 7,7-*Dichlorospiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1'-*cyclopentan*)-6-*one* (10). Dichloroacetyl chloride (12.276 g, 83.1 mmol) was allowed to react with spiro[4.4]nona-6,8-diene (9) [12] to give the tricyclic dichloro-ketone (14.533 g, 68.5%) as a pale yellow liquid, b.p. 111 °C at 3.5 mmHg (Found: C, 57.25; H, 5.35. $C_{11}H_{12}Cl_2O$ requires C, 57.16; H, 5.23%), $\nu_{max.}$ (neat) 1 806 cm^{-1}; δ 0.67—2.30 (8 H, m, cyclopentyl), 3.87 (1 H, d, *J* 7.1 Hz, 5-H), 4.11 (1 H, ddd, *J* 7.1, 2.0, and 1.3 Hz, 1-H), 5.71 (1 H, dd, *J* 5.8 and 2.0 Hz, 2-H), and 5.97 (1 H, dd, *J* 5.8 and 1.3 Hz, 3-H). The compound gave one spot by t.l.c.

(e) 2,2-*Dichloro*-2a,7a-*dihydrospiro*-[7H-*cyclobut*[a]*indene*-7,1'-*cyclopentan*)-1(2H)-*one* (19). Dichloroacetyl chloride (7.12 g, 48.3 mmol) was allowed to react with spiro[cyclopentane-1,1'-[1*H*]-indene] (18) to give, after separation on a silica-gel column with benzene–hexane (1 : 1) as an eluant, the dichloro-ketone (19) (6.15 g, 45.3%) as colourless plates, m.p. 67.0—67.5 °C (from hexane) (Found: C, 64.3; H, 5.2. $C_{15}H_{14}Cl_2O$ requires C, 64.07; H, 5.02%), $\nu_{max.}$ (neat 1 798 cm^{-1} (C=O); δ 1.66—2.20 (8 H, m, cyclopentyl), 4.09 (1 H, d, *J* 7.7 Hz, 7a-H), 4.50 (1 H, d, *J* 7.7 Hz, 2a-H, and 7.17—7.53 (4 H, m, aromatic); $\lambda_{max.}$ (MeOH) 238 (log ε 3.09), 245sh (3.08), 250sh (3.04), 255sh (2.97); 257sh (2.92), 261sh (2.94), 269sh (3.07), 276 (3.12), 279sh (3.10), 310sh (1.98), and 322 nm (1.99).

General Procedure for Hydrolysis of the Spiro-adducts.— A mixture of the spiro-adduct, sodium hydroxide (25 g, 0.625 mol), glacial acetic acid (150 ml), and water (15 ml) was heated for 24 h; the reaction mixture was then poured into water (500 ml) and extracted with dichloromethane (150 ml × 4). The extract was washed with brine (100 ml × 7), and dried over anhydrous magnesium sulphate overnight. The dichloromethane was then removed in a rotary evaporator.

(a) The spiro-dichloro-ketone (2a) (5.69 g, 28 mmol) in this way gave a yellow oil (1.431 g), b.p. 170 °C at 1 mmHg, which was chromatographed on a silica gel (60 g) column with ether as an eluant to give 3-(2'-acetoxyethyl)-1*H*-cycloheptatrien-1-one (3a) (95 mg, 1.63%) as colourless needles, m.p. 53.0—54.0 °C (from hexane) (Found: C, 63.45; H, 5.95. $C_{11}H_{12}O_4$ requires C, 63.45; H, 5.81%), $\nu_{max.}$ 3 100 (OH), 1 728 (C=O), 1 608 (C=C), and 1 592 cm^{-1} (C=O); δ 2.01 (3 H, s, methyl), 3.16 (2 H, t, *J* 6.6 Hz, 1'-H), 4.37 (2 H, t, *J* 7.0 Hz,

2′-H), 6.77—7.42 (4 H, m, aromatic) and 7.58 (1 H, s, hydroxy, exchangeable with deuterium); $\lambda_{max.}$ (EtOH) 236 (log ε 4.28), 322 (3.70), 338.8 (3.63), 354 (3.66), 370 (3.61), and 396sh nm (2.99). Successive elution with acetone gave 2,3-dihydro-8*H*-cyclohepta[*b*]furan-8-one (4a) (1.336 g, 32.5%) as colourless needles, m.p. 53.0—54.0 °C (from hexane) (Found: C, 72.6; H, 5.15. $C_9H_8O_2$ requires C, 72.96; H, 5.44%), $\nu_{max.}$ 1 619 (C=C) and 1 562 cm^{-1} (C=O); δ (200 MHz) 3.45 (2 H, t, 3-H), 4.72 (2 H, t, 2-H), 6.93 (1 H, m, aromatic), 7.15 (1 H, d, *J* 10.2 Hz), and 7.28 (2 H, m); ^{13}C n.m.r. (25 MHz, $CDCl_3$) δ 34.3 (C-3), 70.1 (C-2), 128.0, 129.0 (C-3a), 132.0, 135.9, 138.2, 165.0 (C-8a), and 175.8 (C-8). The picrate of (4a) formed yellow plates, m.p. 149—150 °C (from aqueous ethanol) (Found: C, 47.85; H, 2.85; N, 11.0. $C_{15}H_{11}N_3O_9$ requires C, 47.75; H, 2.95; N, 11.15%). The styphnate of (4a) formed yellowish brown needles, m.p. 173—174 °C (from aqueous ethanol) (Found: C, 45.8; H, 2.7; N, 10.35. $C_{15}H_{11}N_3O_{10}$ requires C, 45.81; H, 2.82; N, 10.69%). The copper salt of (3a) formed green plates, m.p. 215—216 °C (from chloroform) [Found: C, 55.3; H, 4.8. $(C_{11}H_{11}O_4)_2Cu$ requires C, 55.29; H, 4.64%]. The acetate (3a) (416 mg, 1.99 mmol) was treated in the similar way to give the dihydrocycloheptafuran (4a) (129 mg, 43.7%) and recovery of (3a) (10 mg).

(b) The spiro-dichloro-ketone (2b) and (2c) (5 g, 25.3 mmol) was treated as just described to give recovery of (2b) and (2c) (178 mg), 3-(2′-acetoxypropyl)-1*H*-cycloheptatrien-1-one (3b) (617 mg, 12.8%) as pale yellow plates, m.p. 65.0—66.0 °C (from hexane) (Found: C, 64.7; H, 6.4. $C_{12}H_{14}O_4$ requires C, 64.85%; H, 6.35%), $\nu_{max.}$ (KBr) 3 600—3 300 (OH), 3 225 (OH), 1 723 ($OCOCH_3$), 1 615 (C=C), and 1 601 cm^{-1} (C=O); δ 1.36 (3 H, d, *J* 6.3 Hz, CH_3), 1.94 (3 H, s, $COCH_3$), 3.07 (2 H, m, 3′-H), 5.27 (1 H, m, 2′-H), 6.77—7.64 (4 H, m, aromatic), and 9.29 (1 H, OH); and 2-methyl-2,3-dihydro-8*H*-cyclohepta[*b*]furan-8-one (4b) (1.098 g, 26.7%) as a yellow oil, b.p. 150 °C at 0.5 mmHg (Found: C, 74.35; H, 6.25. $C_{10}H_{10}O_2$ requires C, 74.05; H, 6.22%), $\nu_{max.}$ 1 615 (C=C) and 1 557 cm^{-1} (C=O); δ 1.52 (3 H, d, *J* 6.5 Hz, CH_3), 3.32 (2 H, m, 3-H), 5.09 (1 H, m, 2-H), and 6.50—7.50 (4 H, m, aromatic). The picrate of (4b) formed yellow plates, m.p. 151—152 °C (from aqueous ethanol) (Found: C, 48.95; H, 3.3; N, 10.6. $C_{16}H_{13}N_3O_9$ requires C, 49.11; H, 3.35; N, 10.74%).

(c) The spiroindene adduct (6) (7.014 g, 27.71 mmol) was treated similarly and the product was chromatographed on a silica-gel (40 g) column with ether as an eluant to give 5-(2′-acetoxyethyl)-7*H*-benzocycloheptene (7) (20 mg, 5.9%) as yellow plates, m.p. 134—135 °C (from benzene–hexane) (Found: C, 69.6; H, 5.76. $C_{15}H_{14}O_4$ requires C, 69.75; H, 5.46%), $\nu_{max.}$ 3 200 (OH), 1 727 ($OCOCH_3$), 1 632 (C=C), and 1 563 cm^{-1} (C=O); δ 2.07 (3 H, s, $COCH_3$), 3.46—3.70 (2 H, m, CH_2O), 4.34—4.60 (2 H, m, $ArCH_2$), 7.15 (1 H, d, *J* 12.1 Hz, 8-H), 7.83 (1 H, d, *J* 12.1 Hz, 9-H), 7.48—7.97 (3 H, m, aromatic), 8.33 (1 H, d, *J* 8.0 Hz, aromatic), and 9.01 (1 H, s, OH); $\lambda_{max.}$ (EtOH) 241 (log ε 4.45), 244 (4.45), 2.68 (4.35), 279 (4.66), 315sh (3.70), 370 (3.61), and 390sh nm (3.53); successive elution with acetone gave 1,2-dihydro-4*H*-benzo[4,5]cyclohepta[2,3-*b*]furan-4-one (8) (448 mg, 81.7%) as pale brown needles, m.p. 175—176 °C (from benzene–hexane) (Found: C, 78.45; H, 5.25. $C_{13}H_{10}O_2$ requires C, 78.77; H, 5.09%), $\nu_{max.}$ 1 612 (C=C) and 1 583 cm^{-1} (C=O); δ 3.45—3.80 (2 H, m, $ArCH_2$), 4.53—4.90 (2 H, m, OCH_2), 6.95 (1 H, d, *J* 12.8 Hz, 5-H), 7.62 (1 H, d, *J* 12.8 Hz, 6-H), and 7.15—7.90 (4 H, m, aromatic); $\lambda_{max.}$ (EtOH) 240 (log ε 4.34), 247.5 (4.33), 252 (4.33), 280 (4.69), 292.5 (4.23), 320 (3.70), 336.5 (3.74), 370 (3.66), and 380sh nm (3.63). The 2,4-DNP of (8) formed a brown powder, m.p. 275 °C (washed with ether) (Found: C, 60.5; H, 3.65; N, 14.3. $C_{19}H_{14}N_4O_5$ requires C, 60.32; H, 3.73; N, 14.81%). The picrate of (8) formed yellow plates, m.p. 133.5—135.0 °C (washed with ether) (Found: C, 53.4; H, 2.95; N, 9.5. $C_{19}H_{13}N_3O_9$ requires C, 53.40; H, 3.07; N, 9.63%). The acetate (7) was similarly treated to give (8) (135 mg, 81.8%).

(d-1) The spiro-adduct (10) (4.622 g, 20 mmol) was similarly refluxed for 4 h to give 6-hydroxy-1,2,3,4-tetrahydro-7*H*-benzocyclohepten-7-one (16) [14] (146 mg, 4.13%) (Found: C, 75.15; H, 6.95. $C_{11}H_{12}O_2$ requires C, 74.97; H, 6.86%) as pale yellow needles, m.p. 128—129 °C (from hexane), $\nu_{max.}$ 3 225 (OH), 1 618 (C=C), and 1 551 cm^{-1} (C=O); δ 1.78 (4 H, m, $ArCH_2$), 2.79 (4 H, m, CH_2), 7.23 (3 H, m), 7.25 (1 H, s, OH); ^{13}C n.m.r. (50.3 MHz, $CDCl_3$) δ 21.76 (CH_2), 21.90 (CH_2), 33.30 ($ArCH_2$), 34.47 ($ArCH_2$), 122.59, 126.52, 138.20 (C-1a or C-4a), 141.74, 146.92 (C-4a or C-1a), 163.59 (C-6), and 174.68 (C-7); $\lambda_{max.}$ (cyclohexane) 237 (log ε 4.46), 308sh (3.08), 323 (3.88), 343sh (3.78), 357 (3.82), and 375 nm (3.72); and spiro-[4.6]undeca-8,10-diene-6,7-dione (14) (2.323 g, 65.9%) as a yellow oil, b.p. 72 °C at 1.5 mmHg (Found: C, 75.3; H, 6.95. $C_{11}H_{12}O_2$ requires C, 74.97; H, 6.86%), $\nu_{max.}$ 1 716 (C=O), 1 656 (C=O), and 1 578 cm^{-1} (C=C); δ 1.0—2.8 (8 H, m), and 5.5—7.1 (4 H, m); ^{13}C n.m.r. (50.3 MHz, $CDCl_3$) δ 24.31 (C-2 and C-3), 33.56 (C-1 and C-4), 58.94 (C-5), 124.49, 124.79, 140.52, 144.69, 192.91 (C-7), and 198.86 (C-6); $\lambda_{max.}$ 263sh (log ε 3.26), 310 (3.52), 328sh (3.47), and 450 (2.42). The copper salt of (16) formed moss green fine needles, m.p. 276—277 °C (from benzene) (Found: C, 63.95; H, 5.5. $(C_{11}H_{11}O_2)_2Cu$ requires C, 63.83; H, 5.35%). The copper salt of (16) (356 mg, 862 mmol) was dissolved in chloroform (40 ml) and treated with hydrogen sulphide gas to give the tetrahydrobenzocycloheptene (16) (222 mg, 74.5%) as pale yellow needles, m.p. 128—129 °C (from hexane). A mixture of the spiro-diketone (14) (187 mg, 1.06 mmol), *o*-phenylenediamine, and methanol (6 ml) was refluxed for 24 h; the solvent was removed and the residue was chromatographed on a silica-gel (13 g) column with dichloromethane as an eluant to give the quinoxaline derivative (17) (155 mg, 62.4%) as a yellow oil, b.p. 80 °C at 1 mmHg (Found: C, 82.1; H, 6.5; N, 11.05. $C_{17}H_{16}N_2$ requires C, 82.22; H, 6.50; N, 11.28%); $\nu_{max.}$ (neat) 1 632 cm^{-1}; δ 1.17—2.84 (8 H, m, cyclopentyl), 5.77—7.50 (4 H, m), and 7.50—8.30 (4 H, m); $\lambda_{max.}$ (MeOH) 234 (log ε 4.28) and 346 nm (3.92). The picrate of the quinoxaline derivative (17) formed orange red plates (from methanol), m.p. 154—155 °C (Found: C, 58.0; H, 4.3; N, 14.35. $C_{23}H_{19}N_5O_7$ requires C, 57.86; H, 4.01; N, 14.67%).

(d-2) A mixture of the spiro-adduct (10) (4.017 g, 17.4 mmol), triethylamine (20 g), glacial acetic acid (20 g), and water (4 g) was stirred at room temperature for 43 h. The reaction mixture was poured into water (200 ml) and extracted with methylene dichloride (60 ml × 3); the organic phase was then washed with water and dried over anhydrous magnesium sulphate. On a silica-gel column with methylene dichloride as an eluant four products were separated in the following order: recovered (10) (940 mg, 23.4%), 5-acetoxy-7-*exo*-chlorospiro(bicyclo[3.2.0]hept-2-ene-4,1′-cyclopentan)-6-one (12) (528 mg, 11.9%) as a yellow oil, b.p. 95 °C at 1 mmHg (Found: C, 61.6; H, 6.15. $C_{13}H_{15}ClO_3$ requires C, 61.29; H, 5.93%), $\nu_{max.}$ (neat) 1 804 (C=O) and 1 734 cm^{-1} ($OCOCH_3$); δ 1.0—2.2 (8 H, m, cyclopentyl), 2.13 (3 H, s, CH_3), 4.00 (1 H, dd, *J* 9.0 and 2.5 Hz, 1-H), 5.4—6.5 (3 H, m, 2-H, 3-H, and 7-H), 5-hydroxy-7-*exo*-chlorospiro(bicyclo-[3.2.0]hept-2-ene-4,1′-cyclopentan)-6-one (13) (712 mg, 19.2%) as colourless needles, m.p. 90—91 °C (from hexane) (Found: 62.4; H, 6.15. $C_{11}H_{13}ClO_2$ requires C, 62.12; H, 6.16%), $\nu_{max.}$ 3 570 (OH) and 1 794 cm^{-1} (C=O); δ 1.0—2.7 (8 H, m, cyclopentyl), 3.18 (1 H, dd, *J* 7.0 and 1.9 Hz, 1-H), 3.67 (1 H, s, OH), 4.21 (1 H, s, 7-H), and 5.3—6.1 (2 H, m, 2-H and 3-H), the spiro-diketone (14) (190 mg, 6.20%), and a mixture of two kinds of tropolones, which were separated by recrystallisation of their copper salts and successive treatment

with hydrogen sulphide to give 6-hydroxy-1,2,3,4-tetrahydro-7*H*-benzocyclohepten-7-one (16) (157 mg, 5.12%) and 6-hydroxy-1,2,3,4-tetrahydro-5*H*-benzocyclohepten-5-one (15) (46 mg, 1.51%) as colourless needles, m.p. 77 °C (from hexane), $\nu_{max.}$ 3 445 (OH), 1 625 (C=C), 1 604 (C=O), 1 585, 1 530, and 1 501 cm^{-1}; δ 1.78 (4 H, m, CH_2), 2.90 (4 H, m, $ArCH_2$), 6.72—7.38 (3 H, m, aromatic), and 8.83 (1 H, OH); $\lambda_{max.}$ (cyclohexane) 240sh (log ε 4.38), 243—246 (4.39), 309.5sh (3.71), 322.5—324 (3.80), 336sh (3.76), 343.5—353 (3.71), 357—361.5 (3.65), and 368—370 nm (3.64). The copper salt of (15) formed moss-green fine needles, m.p. 301 °C (decomp.) (from benzene) [Found: C, 63.75; H, 5.4. $(C_{11}H_{11}O_2)_2Cu$ requires C, 63.83; H, 5.35%]. A mixture of the hydroxy-ketone (13) (660 mg, 3.1 mmol) was similarly treated at 40 °C for 48 h to give a mixture of the benzocycloheptenones (15) and (16) (68 mg, 1.2%) and the spiro-diketone (14) (5 mg).

(e-1) The spiroindene adduct (19) (4.00 g, 14.2 mmol) was similarly treated and chromatographed on a silica-gel column with hexane–benzene (1 : 1) as an eluant to give spiro(5*H*-benzocycloheptene-5,1′-cyclopentane)-6,7-dione (22) (1.385 g, 43.3%) as yellow pyramids, m.p. 47.0—48.5 °C (from hexane), b.p. 100 °C at 3×10^{-4} mmHg, *m/z* (75 eV) 226 (M^+), 198 ($M^+ - CO$, 50%), 170 ($M^+ - 2CO$, 10%), and 150 (100%) (Found: C, 79.65; H, 6.45. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%), $\nu_{max.}$ (neat) 1 712 (C=O), 1 657 (C=O), and 1 606 cm^{-1} (C=C); $\nu_{max.}$ 1 719 (C=O), 1 663 (C=O), and 1 618 cm^{-1} (C=C); δ 1.68—2.74 (8 H, m, cyclopentyl), 6.21 (1 H, d, *J* 12.6 Hz, 8-H), 7.40 (1 H, d, *J* 12.6 Hz, 9-H), 7.34—7.41 (4 H, m, aromatic); ^{13}C n.m.r. (20 MHz, $CDCl_3$) δ 23.4 (C-3′, C-4′), 33.0 (C-2′, C-5′), 62.1 (C-1′), 124.3 (C-8), 126.6, 128.0, 131.5, 133.2 (C-4a or C-9a), 134.8, 139.4 (C-4a or C-9a), 147.2 (C-9), 191.3 (C-7), and 200.7 (C-6); $\lambda_{max.}$ (MeOH) 225 (log ε 3.78), 243 (3.94), 250sh (3.93), 255sh (3.79), 257sh (3.66), 260sh (3.57), 265sh (3.33), 277sh (3.11), and 316 nm (3.77).

(e-2) The spiroindene adduct (19) (500 mg, 1.77 mmol) was treated in the similar manner as described above except that the reaction temperature was 85 °C; silica-gel column chromatography with hexane as an eluant gave, initially, recovery of (20) (59.7 mg, 11.9%) and then 7a-acetoxy-2-*exo*-chloro-2a,7a-dihydrospiro(7*H*-cyclobut[*a*]indene-7,1′-cyclopentan)-1(2*H*)-one (20) (11.6 mg, 2.4%) as colourless needles, m.p. 145—147.5 °C (from hexane), *m/z* (75 eV) 278 ($M^+ + 2$, 33%), 276 (M^+, 100), and 241; $\nu_{max.}$ 1 792 (C=O) and 1 730 cm^{-1} (C=O); δ 1.93 (8 H, m, cyclopentyl), 2.15 (3 H, s, $COCH_3$), 4.52 (1 H, d, *J* 9.0 Hz, 2a-H), 5.66 (1 H, d, *J* 9.0 Hz, 2-H), and 7.26 (4 H, m, aromatic), and with benzene as an eluant gave 2-*exo*-chloro-7a-hydroxy-2a,7a-dihydrospiro-(7*H*-cyclobut[*a*]indene-7,1′-cyclopentan)-1(2*H*)-one (143 mg, 30.8%) as colourless pyramids, m.p. 117—118 °C (from hexane), *m/z* (75 eV) 264 ($M^+ + 2$, 34.7%) and 262 (M^+, 100) (Found: C, 68.6; H, 5.95. $C_{15}H_{15}ClO_2$ requires C, 68.57; H, 5.73%), $\nu_{max.}$ (KBr) 3 300 (OH) and 1 770 cm^{-1} (C=O); δ 1.85—2.58 (8 H, m, cyclopentyl), 3.51 (1 H, s), 3.80 (1 H, s), 4.21 (1 H, s), and 7.02—7.30 (4 H, m, aromatic); $\lambda_{max.}$ (EtOH) 249 (log ε 2.60), 255 (2.65), 264 (2.73), 268sh (2.72), 274 (2.72), 286sh (2.25), and 308 nm (2.44). A mixture of the diketone (22) (135 mg, 0.597 mmol), *o*-phenylenediamine (88.5 mg, 0.818 mmol), and methanol (23 ml) was refluxed for 6 h at 90 °C to give the quinoxaline derivative (23) (173 mg, 96.8%) as colourless pyramids, m.p. 135—136 °C (from methanol) (Found: C, 84.85; H, 6.0; N, 9.35. $C_{21}H_{18}N_2$ requires C, 84.53; H, 6.08; N, 9.33%), $\nu_{max.}$ (neat) 1 630 cm^{-1} (C=N); δ 1.30—3.20 (8 H, m, cyclopentyl), 7.00—8.10 (8 H, m, aromatic), 7.61 (1 H, d, *J* 9.8 Hz, seven-membered ring), and 8.30 (1 H, d, *J* 9.8 Hz, seven-membered ring close to nitrogen).

1-*Methylspiro*[2.4]*hepta*-4,6-*diene* (1b).—2,3-Dibromopropane (540 g, 2.67 mol) was added to a mixture of cyclopentadiene (176 g, 2.67 mol), sodium hydroxide solution (50%, 500 ml), and cetyltrimethylammonium chloride during 2 h, when the reaction temperature was kept at 30—50 °C. The reaction mixture was filtered with the aid of Celite, diluted with an equal volume of water, and extracted with ether (300 ml × 3); the organic phase was washed with brine and dried over anhydrous magnesium sulphate. The distillation gave a mixture of unchanged 2,3-dibromopropane (199 g, 36.9%) and the spirocyclopropane (1b) (49 g, 17.3%), δ 1.25—2.48 (6 H, m, methyl and cyclopropyl), 5.91—6.71 (4 H, m, olefinic). This mixture was used for the addition reaction of dichloroketen.

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