Unusual Formation of Tricyclic Annulenediones: Diatropic Cationic 10π-Electron Species in D_2SO_4

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Intramolecular oxidative coupling of 1-(3-oxopent-1-en-4-ynyl)-6-(1-oxoprop-2-ynyl)cyclohepta-1,3,5-triene 2 under the Glaser conditions unexpectedly afforded two tricyclic annulenediones. The unusual structures were determined by X-ray crystallographic analysis of the compounds. These annulenediones are atropic in $CDCl_3$, but exhibited diatropicity in CF_3CO_2D and D_2SO_4 ascribable to the formation of cationic 10π-electron species.

We have recently reported that in attempted cyclization of a series of diketones 1–9 carrying terminal acetylene groups under the Glaser conditions compounds 3, 5 and 7 gave, unexpectedly, the annulenediones 10, 11 and 12, respectively, containing a 1,4-dichlorobutatriene moiety. We showed that these annulenediones 10–12 exhibited strong diatropicity in D_2SO_4 due to dicationic 14π-, 18π- and 22π-electron species respectively.[1]

Thus, the Glaser cyclization of compounds 1–9 succeeded when the side-chains at the 1 and 6 positions of the cycloheptatriene ring were of the same length except for the shortest and the longest members examined, 1 and 9, while
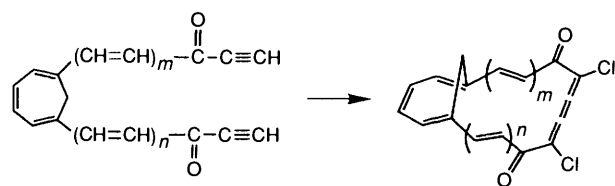
1 m = n = 0
2 m = 1, n = 0
3 m = n = 1
4 m = 2, n = 1
5 m = n = 2
6 m = 3, n = 2
7 m = n = 3
8 m = 4, n = 3
9 m = n = 4

[16]-10 m = n = 1
[20]-11 m = n = 2
[24]-12 m = n = 3

the diketones 4, 6 and 8, carrying side chains of differing lengths, afforded no cyclization products.

The diketone 2 behaved differently in that, whilst affording two reaction products under the Glaser conditions, neither was the desired didehydromethano[14]annulenedione 16. Since the structures of the two compounds were not easily elucidated by spectroscopy, an X-ray crystallographic analysis of each was performed, which revealed that they were tricyclic annulene-diones 13 and 14 containing two and three chlorine atoms, respectively.

This paper deals with the preparation, characterization and properties of compounds 13 and 14.

Results and Discussion

Preparation.—The starting diketone 2 was prepared as reported.[1b] At first, an oxidative coupling of compound 2 was

attempted under the Glaser conditions[2] by bubbling oxygen through a mixture of compound 2, copper(I) chloride and ammonium chloride in aqueous ethanol–benzene containing conc. hydrochloric acid at 60 °C. Chromatography of the product on silica gel afforded two compounds in 0.8 and 2.1% yields, which were later shown to be compounds 13 and 14, respectively.

The ^{1}H and ^{13}C NMR spectra of the two compounds were incompatible with the assignment of structure 16, didehydro-methano[14]annulenedione, to them but failed to allow a correct structural assignment to be made. Therefore we decided to rely on X-ray crystallographic analysis. Although the Glaser coupling reactions were repeated several times to accumulate sufficient of the two compounds, in order to obtain good single crystals for X-ray analysis, the yield of each could not be improved.

When the reaction was carried out without bubbling oxygen through the reaction mixture, the yield of compound 14 slightly increased (3.7%) but compound 13 was absent, instead an acyclic diketone containing two chlorine atoms, 15, being obtained (3.5%).

X-Ray Structural Determination of Compounds 13 and 14.— Single-crystal X-ray crystallographic analyses of compounds 13 and 14 were performed and perspective drawings of their structures are shown in Fig. 1. The analysis reveals that both compounds possess a common tricyclic structure in which a methano[11]annulenone ring is fused with a cyclopentadienone ring. Compound 13 possesses two chlorine atoms which are attached to the cyclopentadienone moiety, while compound 14 has three chlorines, two of which are attached to the five-membered moiety and the remaining one to the [11]annulenone moiety.

^{1}H NMR Spectra of Compounds 13 and 14.—Once the structures of compounds 13 and 14 had been determined by X-ray analysis, their ^{1}H NMR spectra in $CDCl_3$ were found to be completely consistent with the structural assignments. ^{1}H NMR results for compounds 13 and 14 are listed in Table 1 together with those of the closely related compound 17 which was prepared by Vogel *et al.*;[3] the spectra of compound 13 in $CDCl_3$ and in D_2SO_4 are illustrated in Fig. 2. In compound 13, irradiation of the H^A signal at δ 7.86 enhanced the H^1 signal at δ 7.07 and thus all the signals were unambiguously assigned as given in Table 1.

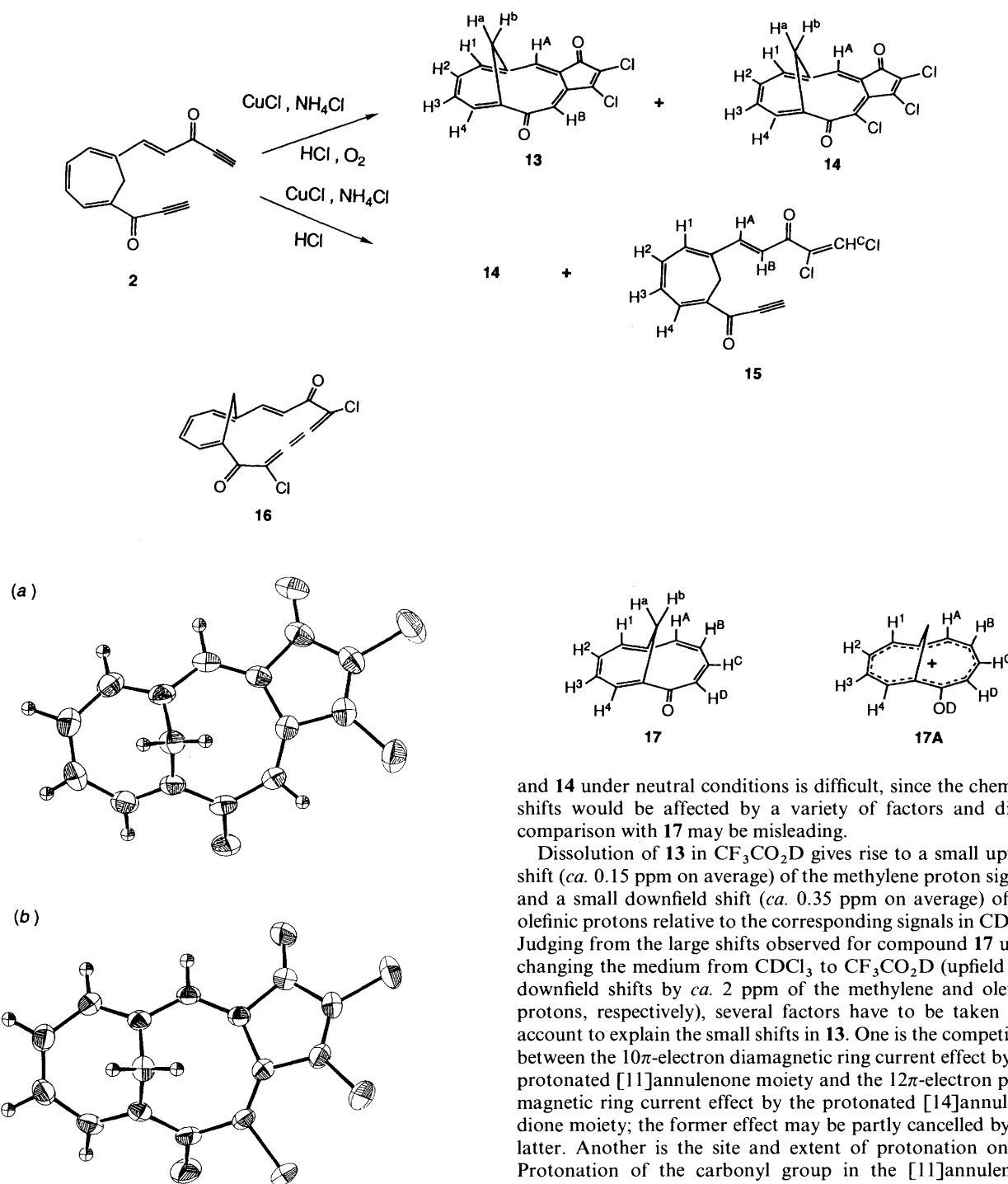Since compounds 13 and 14 contain a methano[11]annul-enone moiety, the bicyclic [11]annulenone 17 would serve as a

Fig. 1 The ORTEP drawings of (a) compound 13 and (b) compound 14

reference compound for the tropic properties of the former. If the whole peripheral π-system participates in conjugation, compounds 13 and 14 would behave as a potential 12π-electron system and be paratropic.

Compound 17 was concluded to be atropic in $CDCl_3$ from its ^{1}H NMR spectral behaviour,[3] but to be diatropic as shown by the ^{1}H NMR spectral data in CF_3CO_2D (Table 1) where it exists as a protonated monocationic 10π-electron species 17A.

Both the methylene and olefinic proton signals of 13 and 14 in $CDCl_3$ appear at a lower field (by $ca.$ 0.5 ppm) than the corresponding signals of 17. Speculation as to the tropicity of 13

and 14 under neutral conditions is difficult, since the chemical shifts would be affected by a variety of factors and direct comparison with 17 may be misleading.

Dissolution of 13 in CF_3CO_2D gives rise to a small upfield shift ($ca.$ 0.15 ppm on average) of the methylene proton signals and a small downfield shift ($ca.$ 0.35 ppm on average) of the olefinic protons relative to the corresponding signals in $CDCl_3$. Judging from the large shifts observed for compound 17 upon changing the medium from $CDCl_3$ to CF_3CO_2D (upfield and downfield shifts by $ca.$ 2 ppm of the methylene and olefinic protons, respectively), several factors have to be taken into account to explain the small shifts in 13. One is the competition between the 10π-electron diamagnetic ring current effect by the protonated [11]annulenone moiety and the 12π-electron paramagnetic ring current effect by the protonated [14]annulenedione moiety; the former effect may be partly cancelled by the latter. Another is the site and extent of protonation on 13. Protonation of the carbonyl group in the [11]annulenone moiety is more likely than that in the cyclopentenone moiety, since the former affords a stable 10π species (13A ⟷ 13A'). Although previous studies have shown that annulenediones predominantly exist as a monocationic species in CF_3CO_2D,[4] the population of the unprotonated neutral species may be significant in the case of 13.

As can be seen from Fig. 2, dissolution of compound 13 in D_2SO_4 induces large shifts of the methylene protons (1.47 ppm on average) and downfield shifts of the olefinic protons (0.85 ppm on average); these results show that strongly diatropic species are formed in this medium, although the diatropicity is still smaller than that of 17 in CF_3CO_2D. Here again the competition between diatropicity and paratropicity and the extent of protonation may affect the extent of the shifts. The ^{1}H NMR spectral behaviour therefore suggests that compound 13 in D_2SO_4 exists predominantly as dicationic species 13B formed

Table 1 ¹H NMR parameters of compounds **13**, **14** and **17** at ambient temperature[a,b]

Compd.	Solvent	H^A	H^B	H^C	H^D	H^a	CH₂	H^b	H^1	H^2	H^3	H^4
17[c]	CDCl₃	5.80			7.50	0.35 d	−0.48 s	3.08 d	5.80			7.50
	CF₃CO₂D	7.80			9.0				7.80			9.0
13	CDCl₃	7.864 br s	7.016 d (0.9)			0.954 d (12.3)		3.461 dt (12.3, 1.4)	7.067 br d (6.3)	7.350 dd (10.6, 6.3)	7.298 dd (10.6, 6.3)	7.508 br d (6.3)
	CF₃CO₂D	8.249 s	7.424 s			0.968 d (12.7)		3.150 d (12.7)	7.427 d (6.7)	7.690 dd (10.8, 6.7)	7.581 dd (10.8, 6.7)	7.860 d (6.7)
	D₂SO₄	8.701 s	7.829 s			0.287 d (13.1)		1.187 d (13.0)	7.981 d (7.9)	8.200 dd (10.5, 7.7)	8.013 dd (10.5, 8.1)	8.503 d (7.9)
14	CDCl₃	7.502 s				0.788 dd (12.0, 0.8)		3.817 dt (12.0, 1.2)	7.012 dd (6.5, 1.0)	7.411 dd (10.6, 6.5)	7.309 dd (10.5, 6.6)	7.648 dt (6.6, 1.0)
	CF₃CO₂D	7.788 s				0.950 d (12.3)		3.749 d (12.3)	7.245 d (7.1)	7.649 dd (10.6, 6.6)	7.508 dd (10.6, 6.8)	7.906 d (6.8)
	D₂SO₄	8.464 s				0.206 d (12.4)		0.864 d (12.4)	8.098 d (8.4)	8.314 dd (9.9, 8.2)	8.135 dd (9.9, 8.6)	8.693 d (8.4)

[a] Obtained at 500 MHz unless otherwise stated. [b] J Values are given in Hz. [c] Obtained at 60 MHz, see ref. 4.
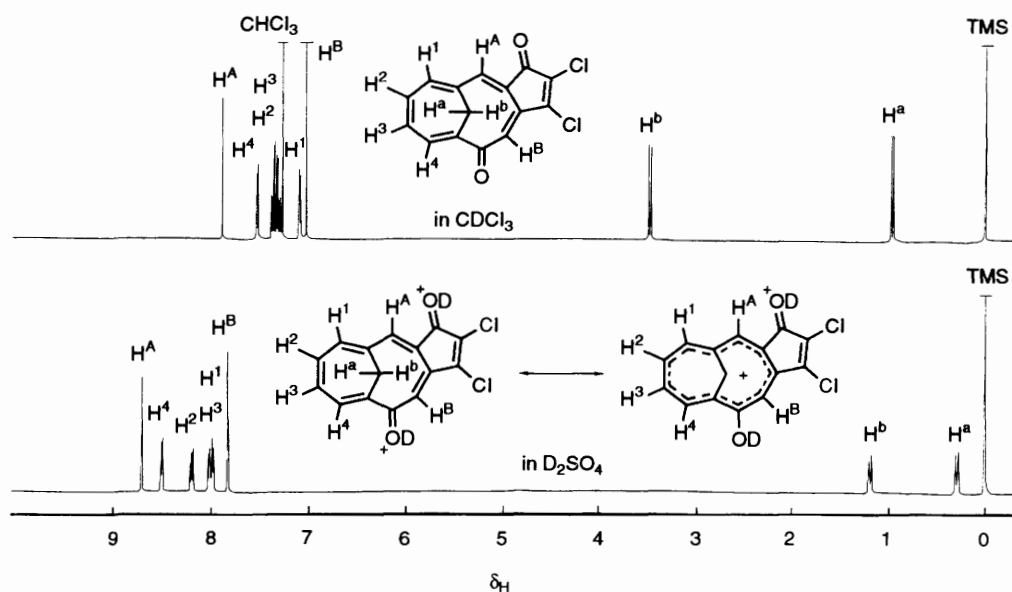
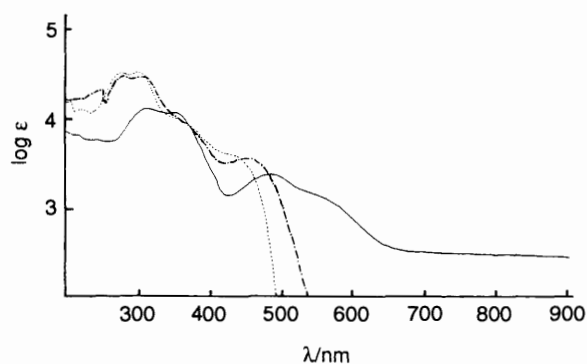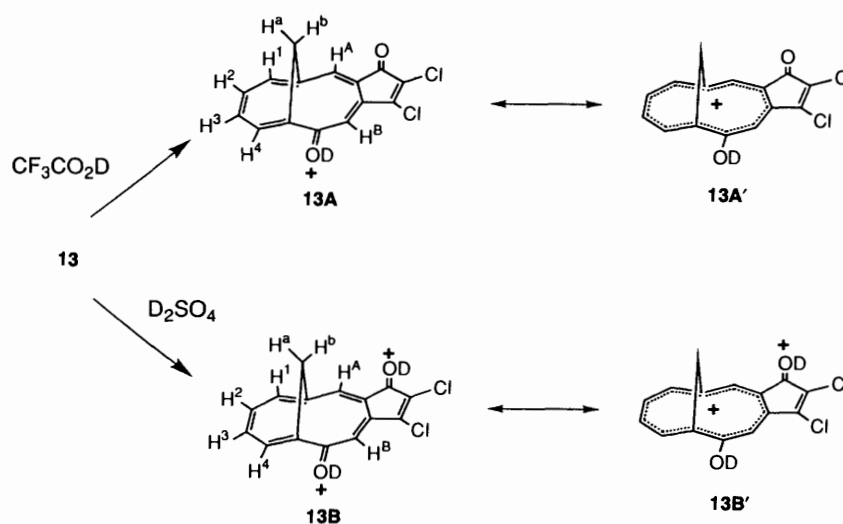**Fig. 2** 500 MHz ^{1}H NMR spectra at 26 °C: (a) in CDCl$_3$ and (b) in D$_2$SO$_4$ of compound **13**

Fig. 3 Electronic absorption spectra of cmpound **14** (– – – –) in THF, (– · — · —) in CF$_3$CO$_2$H and (——) in H$_2$SO$_4$

by protonation of both carbonyl groups and behaves as a 10π-electron diatropic species **13B'** rather than a 12π-electron paratropic species.

As can be seen from Table 1, compound **14** behaves in a similar fashion to compound **13**.

Electronic Spectra of Compounds **13** *and* **14**.—The electronic absorption spectra of compound **14**, determined in tetrahydrofuran (THF), CF$_3$CO$_2$H and H$_2$SO$_4$, are illustrated in Fig. 3. It is evident from Fig. 3 that all the bands of compound **14** show a progressive bathochromic shift as the solvent is changed from THF to CF$_3$CO$_2$H and to H$_2$SO$_4$, the end absorption in H$_2$SO$_4$ appearing toward longer wavelength as compared with that for the spectra in THF and CF$_3$CO$_2$H; this reflects the degree of extended conjugation of the π-electron system in the solvent, as is revealed by their ^{1}H NMR spectra (see above).

Mechanism for the Formation of Compounds **13** *and* **14**.—Pilling and Sondheimer reported formation of chlorine-containing compounds upon attempted cyclization of bis-ethynyl compounds under the Glaser conditions but they failed to characterize the products.[5] Our reports[1] on the synthesis of compounds **10–12** are the first examples of formation of chlorine-containing annulene derivatives, although we were unable to elucidate the mechanistic detail of their formation. Here again, although the mechanism of the formation of compounds **13** and **14** is uncertain, a tentative speculation is presented in Scheme 1.

18

19

21   **20**

22

Scheme 1
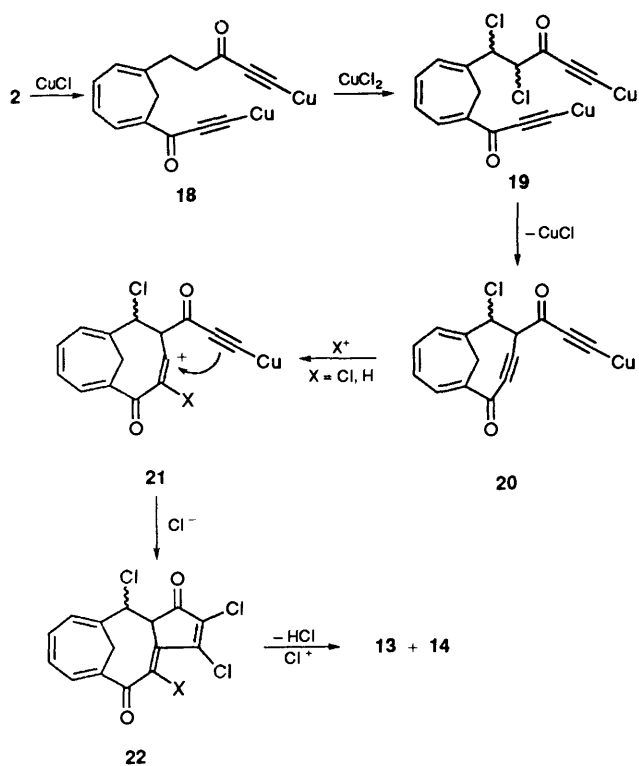
Copper(i) chloride used in the Glaser coupling often contains copper(ii) chloride as an impurity which may chlorinate the initially formed bis[copper(i) acetylide] **18** to give **19**. The dichloro derivative **19** may then cyclize to form **20** with elimination of CuCl. The highly strained intermediate **20** would react with a cationic species X^+ (X = Cl or H) to give a cation **21**, which would cyclize and then react with chloride ion to form a tricyclic species **22**. Elimination of HCl and chlorination of the vinyl copper **21** would then give compounds **13** and **14**. The open-chain product **15** may result from the addition of Cl_2 to the acetylenic bond of **18**.

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO-7300 spectrophotometer as KBr discs; only significant maxima are described. Electronic (UV–VIS) spectra were measured in THF, CF_3CO_2H and H_2SO_4 solutions and run with a Shimadzu 2200A spectrophotometer, and refer to THF solution unless otherwise stated. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. ^1H NMR spectra at ambient temperature were recorded as $CDCl_3$ solutions, unless otherwise specified, with a Bruker AM-500 spectrometer at 500.14 MHz. Internal $SiMe_4$ (TMS) was used as a reference when the solvent was $CDCl_3$ or CF_3CO_2D while external $SiMe_4$ was used when the solvent was D_2SO_4. J Values are given in Hz. ^{13}C NMR spectra were recorded as $CDCl_3$ solution, unless otherwise indicated, on an AM-500 instrument at 125.76 MHz with internal $SiMe_4$ as a reference.

Progress of all reactions was followed by TLC on Merck pre-coated silica gel. Silica gel (Daiso gel 1002 W) was used for column chromatography. Compounds were pre-adsorbed from benzene solution onto the adsorbent before column chromatography. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior

to removal of solvent. Solvents were evaporated under water-pump pressure.

2,3-*Dichloro*-1,5-*dihydro*-6,11-*methanocyclopenta*[11]*annulene*-1,5-*dione* (5,6-*Dichlorotricyclo*[8.4.1.0^{3,7}]*pentadeca*-2,5,7,-10,12,14-*hexaene*-4,9-*dione*) **13** *and* 2,3,4-*Trichloro*-1,5-*dihydro*-6,11-*methanocyclopenta*[11]*annulene*-1,5-*dione* (5,6,8-*Trichlorotricyclo*[8.4.1.0^{3,7}]*pentadeca*-2,5,7,10,12,14-*hexane*-4,9-*dione*) **14**.—A solution of the diketone **2**^{1b} (700 mg, 3.15 mmol) in benzene–ethanol (1:3, 307 cm³) was added dropwise during 1.5 h to a stirred solution of copper(i) chloride (174 g, 1.75 mol), ammonium chloride (278 g), water (769 cm³) and conc. HCl (3.15 cm³) at 64 °C. The mixture was stirred for 30 min at 64 °C whilst gaseous oxygen was bubbled through it. The mixture was then cooled, poured onto water and extracted with dichloromethane. The combined extracts were washed successively with 2 mol dm⁻³ HCl, aq. $NaHCO_3$ and dried. The residual dark red liquid obtained by removal of solvent was chromatographed on silica gel (4.2 × 4.5 cm). The fractions eluted with hexane–benzene (3:7) afforded the *title dione* **14** (21 mg, 2.1%) as pale orange needles, m.p. 181–183 °C (from hexane–benzene); m/z 328 [$(M + 4)^+$, 22%], 326 [$(M + 2)^+$, 66%], 324 (M^+, 68%) and 261 (100) ($C_{15}H_7Cl_3O_2$ requires M, 324); λ_{max}/nm 207 (ε/dm³ mol⁻¹ cm⁻¹ 16 300), 220 (13 100), 278 (32 500) and 299 (32 800) and see Fig. 3; $\lambda_{max}(CF_3CO_2H)$/nm 250 (ε 21 500), 280 (29 600), 306 (29 000), 375sh (8000) and 451 (3600) and see Fig. 3; $\lambda_{max}(H_2SO_4)$/nm 312 (ε 12 500), 352 (11 500), 484 (2400) and 494 (2300) and see Fig. 3; ν_{max}/cm⁻¹ 1711 and 1640 (C=O) and 1593 (C=C); for ^1H NMR data see Table 1; δ_C 184.21 (q, C=O), 182.91 (q, C=O), 154.57 (q), 138.32 (q), 135.75 (t), 133.97 (t), 133.71 (q), 132.75 (t), 132.56 (q), 131.35 (t), 129.93 (t), 128.41 (q), 123.03 (q), 121.16 (q) and 30.24 (s, CH_2); $\delta_C(CF_3CO_2H)$ 190.0 (q, C=O), 189.9 (q, C=O), 159.7 (q), 140.3 (q), 139.8 (t), 138.6 (t), 136.6 (q), 136.2 (t), 135.9 (q), 135.7 (t), 133.7 (t), 130.1 (q), 125.3 (q), 125.1 (q) and 31.74 (s, CH_2); $\delta_C(D_2SO_4)$ 189.73 (q), 177.59 (q), 160.66 (q), 150.54 (q), 146.72 (t), 142.25 (q), 141.37 (t), 140.86 (t), 140.34 (t), 138.34 (q), 137.52 (t), 131.39 (q), 126.83 (q), 122.67 (q) and 30.78 (s, CH_2) (Found: C, 55.6; H, 2.4. $C_{15}H_7Cl_3O_2$ requires C, 55.3; H, 2.2%).

The later fractions eluted with hexane–benzene (1:9) afforded the *title dione* **13** (7.4 mg, 0.81%) as yellow needles, m.p. 204–208 °C (decomp.) (from hexane–dichloromethane); m/z 292 [$(M + 2)^+$, 23%], 290 (M^+, 36%) and 199 (100) ($C_{15}H_8Cl_2O_2$ requires M, 290); λ_{max}/nm 213 (ε 14 100), 233 (12 700), 278sh (26 800), 290 (31 200), 304sh (28 100) and 368 (8100); $\lambda_{max}(H_2SO_4)$/nm 245 (ε 17 700), 275sh (23 500), 300sh (40 900), 320 (50 700), 344 (53 500), 434 (5800) and 510 (3600); ν_{max}/cm⁻¹ 1716 (C=O) and 1618 and 1598 (C=C); for ^1H NMR data see Table 1 and Fig. 2; δ_C 190.12 (q, C=O), 184.01 (q, C=O), 156.81 (q), 139.23 (t), 136.54 (q), 134.80 (q), 134.14 (t), 133.05 (t), 130.80 (t), 129.07 (t), 128.65 (q), 127.29 (t), 125.42 (q), 122.94 (q) and 31.12 (s, CH_2); $\delta_C(CF_3CO_2D)$ 196.4 (q, C=O), 190.7 (q, C=O), 161.3 (q), 144.7 (t), 143.0 (q), 138.9 (t), 137.5 (q), 136.2 (t), 135.3 (t), 134.8 (t), 130.6 (q), 127.7 (t), 127.6 (q), 127.3 (q) and 32.6 (s, CH_2); $\delta_C(D_2SO_4)$ 190.40 (q), 185.81 (q), 160.35 (q), 149.76 (q), 147.18 (t), 144.46 (t), 140.32 (t), 138.37 (t), 137.21 (t), 135.73 (t), 135.63 (q), 127.21 (q), 125.63 (q), 118.59 (q) and 30.40 (s, CH_2) (Found: C, 62.0; H, 3.0. $C_{15}H_8Cl_2O_2$ requires C, 61.9; H, 2.8%).

1-(4,5-*Dichloro*-3-*oxopenta*-1,4-*dienyl*)-6-(1-*oxoprop*-2-*ynyl*)-*cyclohepta*-1,3,5-*triene* **15**.—A solution of the diketone **2** (500 mg, 2.25 mmol) in benzene–ethanol (1:1, 330 cm³) was added dropwise during 3 h to a stirred solution of copper(i) chloride (124 g, 1.25 mol), ammonium chloride (198 g), water (500 cm³) and conc. HCl (2.25 cm³) at 60 °C. After being stirred for 1.5 h at 60 °C, the mixture was worked up as for the isolation of

Table 2 Crystal data and parameters for data collection, structure determination and refinement

	13	14
Empirical formula	$C_{15}H_8Cl_2O_2$	$C_{15}H_7Cl_3O_2$
Formula weight	291.13	325.58
Crystal dimension (mm)	0.4, 0.5, 0.1	0.2, 0.3, 0.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (# 14)	$P2_1/n$ (# 14)
a (Å)	11.691(1)	4.219(2)
b (Å)	7.266(2)	13.479(2)
c (Å)	15.498(1)	23.028(1)
β (°)	108.819(6)	91.26(2)
V (Å^3)	1246.1(3)	1309.1(6)
Z	4	4
D_c (g cm^{-3})	1.552	1.652
$F(000)$	592	656
μ(Mo-Kα) (cm^{-1})	5.12	6.97
Temp. (°C)	21 ± 1	22 ± 1
Scan width (°)	1.26 ± 0.30 tan θ	1.26 ± 0.30 tan θ
$2\theta_{max}$ (°)	55.2	55.1
No. of reflections measured		
Total	3601	3264
Unique	3183	3118
No. of refinement variables	209	204
Final R; R_w	0.041; 0.044	0.044; 0.044

compounds **13** and **14**. The product was chromatographed on silica gel (4.2 × 6.0 cm). The initial fractions eluted with hexane–benzene (3:2) afforded compound **14** (102 mg, 3.7%).

The later fractions eluted with hexane–benzene (1:1) afforded the *dichloro diketone* **15** (86 mg, 3.5%) as yellow needles, m.p. 132–133 °C (from hexane–ether); *m/z* 294 [(M + 2)⁺, 35%], 292 (M⁺, 54%) and 115 (100) ($C_{15}H_{10}Cl_2O_2$ requires *M*, 292); λ_{max}/nm 229 (ε 12 900), 288 (23 100) and 380 (10 200); v_{max}/cm⁻¹ 3262 (C≡CH), 2098 (C≡C), 1668 (C=O), 1623 (C=C) and 987 [(*E*)-HC=CH]; δ_H 7.624 (1 H, d, *J* 6.1, H⁴), 7.344 (1 H, dd, *J* 15.4 and 0.7, Hᴬ), 7.017 (1 H, dd, *J* 11.1 and 6.3, H²), 6.972 (1 H, d, *J* 15.4, Hᴮ), 6.924 (1 H, dd, *J* 11.0 and 6.1, H³), 6.874 (1 H, s, Hᶜ), 6.656 (1 H, d, *J* 6.3, H¹), 3.262 (1 H, s, C≡CH) and 2.880 (2 H, s, CH₂); δ_C 184.92 (q, C=O), 175.66 (q, C=O), 143.87 (t), 139.11 (t), 136.25 (t), 135.73 (q), 133.72 (t), 133.02 (q), 132.09 (q), 131.56 (t), 127.49 (t), 127.07 (t), 79.72 (q, -C≡), 79.33 (t, ≡CH) and 24.54 (s, CH₂) (Found: C, 61.5; H, 3.6. $C_{15}H_{10}Cl_2O_2$ requires C, 61.45; H, 3.4%).

X-Ray Crystallography.—Crystals of compounds **13** and **14** were grown from dichloromethane–hexane. The crystal data

and parameters for data collection, structural determination and refinement are summarized in Table 2. Diffraction data were collected on a Rigaku AFC5R diffractometer and calculations were performed using the TEXSAN program.[6] The structures were solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. Reflection data within $|F_o| > 2\sigma(F_o)$ were used. The function minimized was $\Sigma w(|F_o| - F_c|)^2$ where $w = [\sigma^2(F_o)]^{-1}$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

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