

Cycloadditions of Methano[11]annulenones with Dichloro- and Chloro-ketenes. Preparation of 2*H*-Methanocycloundeca[*b*]furan-2-one Ring Systems

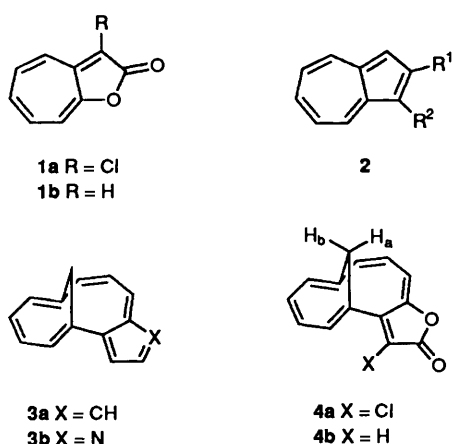
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Cycloaddition of dichloroketene with 3,8-methano[11]annulenone **5** proceeded smoothly to give 3-chloro-2*H*-4,9-methano- and 3-chloro-2*H*-6,11-methano-cycloundeca[*b*]furan-2-ones **4a** and **7a** in good combined yield, while that with 4,9-methano[11]annulenone **6**, gave 3-chloro-2*H*-5,10-methanocycloundeca[*b*]furan-2-one **11a** in modest yield. Reductive elimination of the 3-chloro-substituent of **4a**, **7a** and **11a** was successfully accomplished to give the corresponding parent 2*H*-methanocycloundeca[*b*]furan-2-ones **4b**, **7b** and **11b**, respectively. In a similar reaction using chloroketene, compound **5** gave unsubstituted-, 3-chloroacetyl- and 3-(1-chloroacetoxy-2-chloro)vinyl-2*H*-4,9-methanocycloundeca[*b*]furan-2-ones **4b**, **19** and **20** in good combined yield, while with **6**, only 3-chloroacetyl-2*H*-5,10-methanocycloundeca[*b*]furan-2-one **21** was obtained in modest yield. The reactivity and/or regioselectivity of the cycloadditions were rationalized on the basis of AM1 calculations. An X-ray crystallographic determination of compound **4a** was also carried out.

2*H*-Cyclohepta[*b*]furan-2-one **1b**, which is conveniently prepared starting from the reaction of activated tropones with active methylene compounds,¹ is known to be a valuable synthon, which reacts with enamines to give versatile azulenoid compounds.²⁻³ As for 14π-vinylogues of azulene, Printzbach and Knoche have reported the synthesis of a 5,10-methanocyclopentacycloundecene ring system, which was suggested to have azulenoid character on the basis of its spectroscopic properties.⁴ However, no other methano-bridged isomers such as **3a** have been reported to date. Previously, we have studied



the synthesis and structural properties of methanocycloundeca[*b*]pyrroles, 1-aza-4,9-methano- **3b**, 1-aza-6,11-methano- and 1-aza-5,10-methanocyclopentacycloundecenes.^{5,6} In connection with these studies, we have been interested in the synthesis of the novel 2*H*-methanocycloundeca[*b*]furan-2-one skeleton **4** and related compounds, all of which are 14π-electron vinylogues of **1** and possible precursors for the preparation of methanocyclopentacycloundecene ring systems. Since there is ample justification to view methano[11]annulenone as a vinylogue of tropone,⁷ which undergoes cycloaddition with dichloroketene giving 3-chloro-2*H*-cyclohepta[*b*]furan-2-one **1a**,⁸ our synthetic strategy for compound **4** and its isomers was the reaction of 3,8-methano- and 4,9-methano-[11]annul-

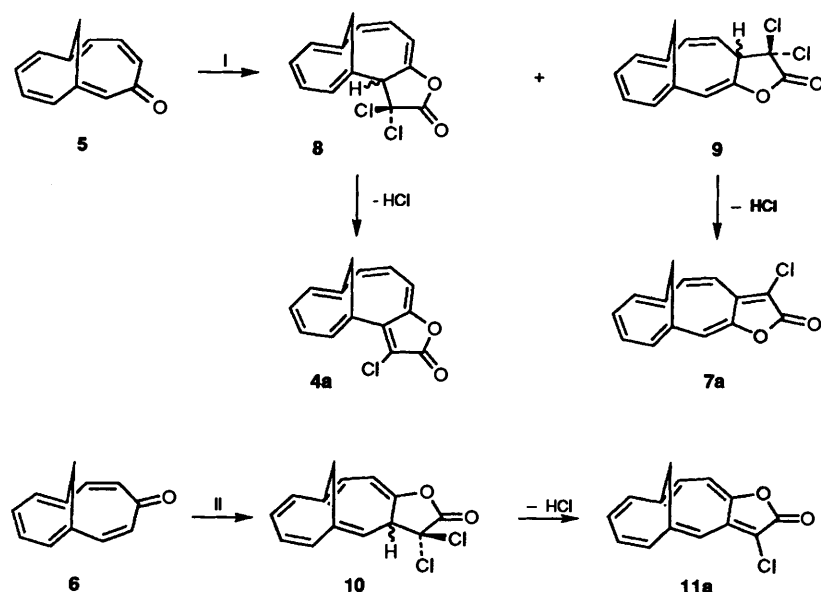
enones **5** and **6**⁷ with dichloroketene and chloroketene.⁹ We describe here the results in detail.

Results and Discussion

Dropwise addition of a solution of dichloroacetyl chloride in CH₂Cl₂ over 20 min at 0 °C to a stirred solution of 3,8-methano[11]annulenone **5** and triethylamine in CH₂Cl₂ under a nitrogen atmosphere resulted in the immediate precipitation of HNEt₃Cl. Compound **5** was relatively reactive and the reaction was complete after a further 10 min at 0 °C. The usual work-up followed by recrystallization and TLC separation afforded compound **4a** (84%) and a mixture of compounds **4a** and **7a** in a ratio of 58:42 (9%), respectively (Scheme 1 and Table 1). However, separation of the mixture by repeated TLC was unsuccessful and the physical data for **7a** have not been obtained (*vide infra*). Compound **6** was less reactive than compound **5**, and stronger conditions were required. After the addition of dichloroacetyl chloride to a stirred solution of compound **6** and triethylamine over 3 h under reflux in CH₂Cl₂, the reaction mixture was refluxed for a further 1 h. The usual work-up followed by TLC gave compound **11a** and unchanged starting material **6** (Scheme 1 and Table 1). The formation of compounds **4a**, **7a** and **11a** is explained by [12 + 2] cycloaddition of dichloroketene with compounds **5** and **6**, respectively. The intermediates **8**, **9** and **10** would be formed by either *endo* or *exo* approach of dichloroketene to the annulene perimeter, and they undergo a facile *trans* dehydrochlorination under the reaction conditions described to give compounds **4a**, **7a** and **11a**, respectively.

In order to gain insight into the reactivity of compounds **5** and **6** and the regioselectivity of the reaction of **5** with dichloroketene, AM1 calculations were performed.⁹ These calculations predict that the heats of formation of compounds **5** and **6** are 53.4 and 51.1 kcal mol⁻¹,[†] respectively, and the HOMO and LUMO coefficients of **5** and **6** were also obtained as depicted in Fig. 1. Thus, compound **5** is predicted to be less stable than **6**. Assuming the transition states of the

[†] 1 cal = 4.184 J.



Scheme 1 Reagents and conditions: i, Cl_2CHCOCl , Et_3N , CH_2Cl_2 , 0°C ; ii, Cl_2CHCOCl , Et_3N , CH_2Cl_2 , reflux

Table 1 Reaction of chlorinated ketenes with methano[11]annulenones

Entry	Methano[11]annulenone	Ketene	Reaction temp.	Product, yield (%)	Recovery (%)
1 ^a	5	Cl_2CCO	0°C	4a, 89; 7a, 4	0
2 ^a	6	Cl_2CCO	Reflux	11a, 25	6, 12
3 ^a	5	ClHCCO	0°C	4b, 14; 19, 10; 20, 40	0
4 ^b	6	ClHCCO	Reflux	21, 9	6, 20

^a The reaction was carried out in CH_2Cl_2 solution. ^b The reaction was carried out in 1,2-dichloroethane solution.

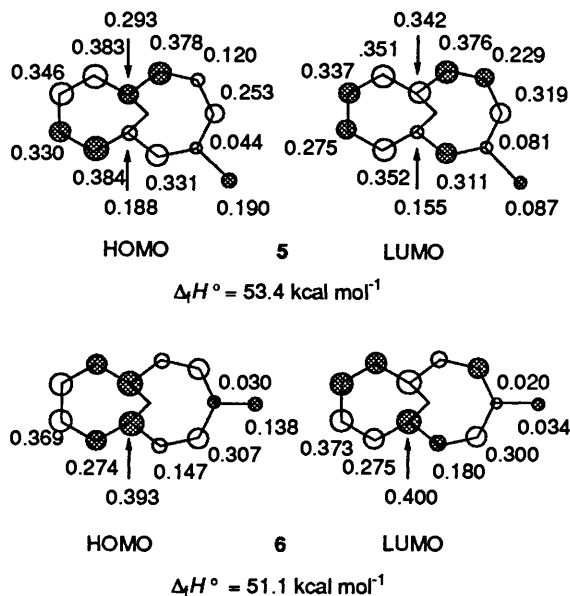


Fig. 1

cycloadditions of **5** and **6** with dichloroketene are similar, the less stable compound **5** would be expected to be more reactive than **6**. This prediction is in agreement with the experimental results. Support for the theoretical prediction has also been obtained in other experimental studies.^{7,10} Furthermore, the cycloaddition of ketene is generally controlled by the LUMO of the ketene and the HOMO of the substrate.¹¹ In the case of compound **5**, a large HOMO coefficient at C-2 compared with that at C-11

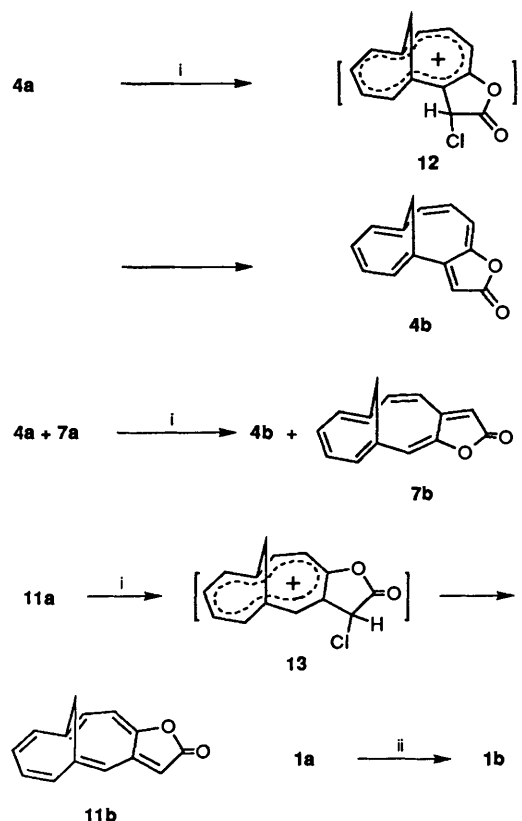
Table 2 Reductive dechlorination of 3-chloro-2*H*-methanocyclo-undeca[*b*]furan-2-ones and 2*H*-cyclohepta[*b*]furan-2-one with NaI in $\text{CF}_3\text{CO}_2\text{H}$

Entry	Starting material	Reaction temp. ^a	Reaction time, t/h	Product, yield (%)	Recovery (%)
1	4a	R.t.	3	4b, 85	4a, 10
2	4a/7a ^b	R.t.	2	4b, 74; 7b, 84	0
3	11a	R.t.	3	11b, 64	11a, 23
4	1a	Reflux	1	1b, 82	0

^a R.t. = room temperature. ^b A mixture of **4a** and **7a** in a ratio of 58:42.

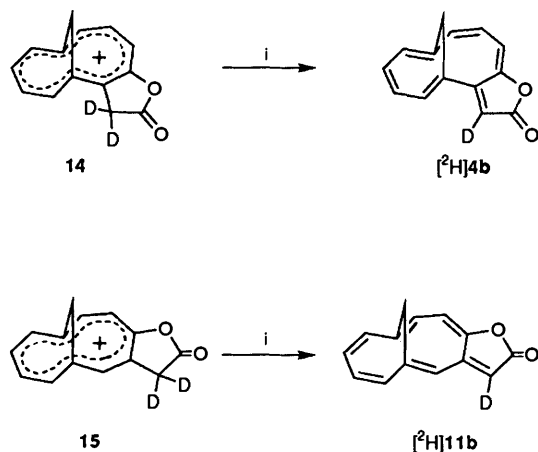
clearly predicts the preferential formation of compound **8** over **9** and therefore **4a** over **7a**. In the case of compound **6**, which has a plane of symmetry, only compound **11a** was obtained in modest yield.

Previously, the reductive elimination of 11-chloro-3,8-methano[11]annulenone has been successfully accomplished by the use of hydrogen iodide.⁷ We used a modified version of this method for the reductive elimination of the chlorine from compounds **4a**, **7a** and **11a** (Scheme 2), and the results are summarized in Table 2. A solution of compound **4a** and an excess of NaI in $\text{CF}_3\text{CO}_2\text{H}$ was stirred at room temperature to give **4b**. In this reaction, the protonation of **4a** gives an aromatic cation **12**,^{7,12} which is reduced by an iodide ion to give **4b**. Similarly, a mixture of compounds **4a** and **7a** was reduced to give **4b** and **7b**. Thus the formation of **7a** in the reaction of **5** with dichloroketene was assessed. In a similar manner, compound **11a** was converted into **11b** possibly *via* intermediate **13** in good yield. The present method was also applicable to the conversion of **1a** into **1b** (Table 2, entry 4).



Scheme 2 Reagents and conditions: i, TFA, NaI, room temp.; ii, TFA, NaI, reflux

The evidence for intermediates **12** and **13** was obtained by ^1H and ^{13}C NMR spectroscopy. The ^1H (Experimental) and ^{13}C NMR (Table 3) of **4b** and **11b** were recorded in $\text{CF}_3\text{CO}_2\text{D}$, and evidence for the existence of the aromatic cations **14** and **15** was obtained. Quenching of the cation with NEt_3 gives [^2H]-labelled compounds [^2H]**4b** and [^2H]**11b**, respectively (Scheme 3). Thus



Scheme 3 Reagents: i, NEt_3

the reductive elimination of the chlorines of compounds **4a** and **11a** seems to proceed *via* the intermediates **12** and **13**, respectively. The conversion of compounds **7a** and **1a** into **7b** and **1b**, respectively, would proceed in a similar way.

The structures of methanocycloundeca[*b*]furan-2-ones **4a**, **b**, **7b** and **11a**, **b** were confirmed by their elemental analyses and ^1H and ^{13}C NMR spectral data. The characteristic ^1H NMR spectral properties of the products are as follows. The average ^1H and ^{13}C chemical shifts of the eleven-membered ring of **4a**

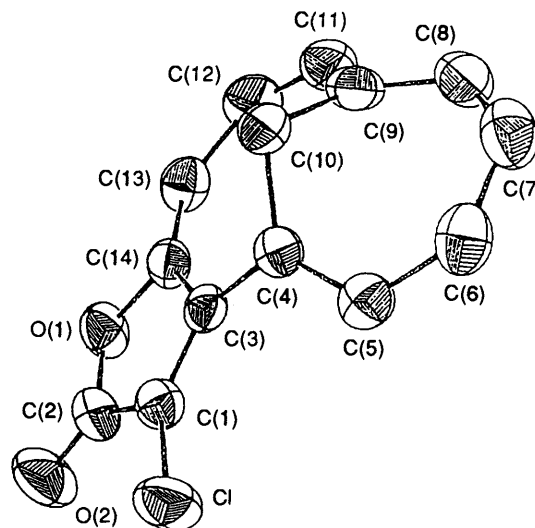


Fig. 2 ORTEP drawing of compound **4a**, with crystallographic numbering scheme

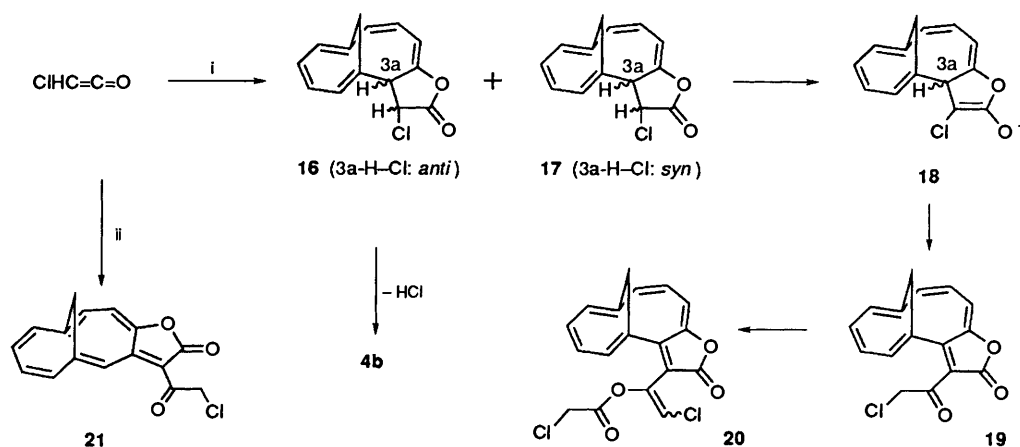
($\delta_{\text{H}}^{\text{av}}$ ca. 7.0 and $\delta_{\text{C}}^{\text{av}}$ 127.5), **4b** ($\delta_{\text{H}}^{\text{av}}$ 6.92 and $\delta_{\text{C}}^{\text{av}}$ 126.7), **7b** ($\delta_{\text{H}}^{\text{av}}$ 7.07 and $\delta_{\text{C}}^{\text{av}}$ 128.3), **11a** ($\delta_{\text{H}}^{\text{av}}$ 6.85 and $\delta_{\text{C}}^{\text{av}}$ 127.1) and **11b** ($\delta_{\text{H}}^{\text{av}}$ 6.83 and $\delta_{\text{C}}^{\text{av}}$ 126.9) are similar to those of **1b** ($\delta_{\text{H}}^{\text{av}}$ 6.82 and $\delta_{\text{C}}^{\text{av}}$ 128.5) (see Experimental section). The average of these ^1H and ^{13}C chemical shifts falls between the values of the delocalized 1,6-methano[11]annulenium ion ($\delta_{\text{H}}^{\text{av}}$ 8.82 and $\delta_{\text{C}}^{\text{av}}$ 144.2)^{4,7,12,13} and bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene ($\delta_{\text{H}}^{\text{av}}$ 5.91 and $\delta_{\text{C}}^{\text{av}}$ 124.5).^{4,7,14} The values for the eleven-membered ring of 3-chloro substituted compounds **4a** and **11a** are shifted slightly downfield compared with the corresponding values of **4b** and **11b**, respectively, indicating the electron withdrawing property of the chlorine. The coupling constants for the resonances of the eleven-membered rings of **4a**, **b**, **7b** and **11a**, **b** suggest the existence of bond-length alternations as found in compound **1b**. The structure of compound **4a** was also confirmed by X-ray crystal-structure analysis (see Experimental section and Fig. 2), which indicates a bond-length alternation in compound **4a**. Furthermore the ^{13}C chemical shifts of C-3 for compounds **4a**, **b**, **7b** and **11a**, **b** appear at relatively higher field than for compound **1b** (Table 3),³ suggesting a high electron density at C-3 leading to the formation of aromatic cations such as **14** and **15**. In view of these data the chemical properties of compounds **4a**, **b**, **7b** and **11a**, **b** are expected to be similar to those of compounds **1a**, **b**.^{15,16}

The cycloaddition of compounds **5** and **6** with chloroketene differed from that with dichloroketene. The reaction of chloroketene with compound **5** at 0°C and the usual work-up followed by purification through TLC resulted in the formation of compounds **4b**, **19** and **20** (Scheme 4) (Table 1, entry 3). The yield of **4b** was not increased by changing the ratio of chloroketene:**5**. Furthermore, in contrast to the reactions of 2*H*-cyclohepta[*b*]thiophene,¹⁷ the reaction of isolated **4b** with chloroketene or chloroacetyl chloride-pyridine under similar conditions did not give compounds **19** and/or **20**, and unchanged **4b** was recovered. Thus **4b** is clearly not an intermediate in the formation of **19** and **20**. Considering either *endo* or *exo* approach of the ketene, the large chlorine of chloroketene is orientated away from the annulene perimeter to give intermediate **17** (*syn* arrangement of 3a-H and Cl) preferentially over **16** (*anti* arrangement of 3a-H and Cl). The minor intermediate **16** undergoes facile *trans* dehydrochlorination to give **4b**. In the intermediate **17**, keto-enol tautomerization seems to take preference over *cis* dehydrochlorination and the enolate anion **18** reacts with chloroketene or chloroacetyl chloride under the reaction conditions to give **19**. The *O*-acetylation of **19** then gives compound **20**. The

Table 3 ^{13}C NMR data of 2*H*-methanocycloundeca[*b*]furan-2-ones^a and protonated species^b

Compd.	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	Remaining carbons ^c
1b	169.5	98.7	127.9	135.4	130.5	132.5	113.8						153.2, 158.4, (C-3a, 8a)
4a	164.4	113.4	— ^d	128.4	131.2	132.5	127.8	— ^d	139.1	121.1	112.2	32.1	117.9, 127.3, 146.6, 147.6
4b	169.0	108.6	— ^d	127.6	131.2	132.0	125.8	— ^d	138.1	121.2	111.3	31.7	119.8, 127.2, 148.9, 157.2
7b	168.6	114.5	121.3	138.8	— ^d	126.7 ^e	(132.0, 132.4)	127.0 ^e	— ^d	120.5	37.5		123.0, 126.5, 149.0, 150.1
11a	163.6	109.1	122.9	— ^d	134.5	128.6	129.6	132.4	— ^d	126.4	115.2	33.8	142.2, 142.8, 145.0, 150.0
11b	168.6	105.8	124.0	— ^d	132.4	129.0	128.2	134.3	— ^d	126.1	114.4	33.2	141.4, 141.6, 151.9, 153.3
19	167.7	— ^d	— ^d	(132.0, 132.9, 134.0, 134.7)				— ^d	143.7	123.3	117.9	30.7	113.2, 120.2, 130.1, 148.7, 159.0, 187.0 (CO), 50.5 (CH ₂ Cl)
20	165.9	— ^d	— ^d	129.2	130.9	132.7	128.6	— ^d	139.8	121.1	113.1	31.7	114.5, 119.9, 128.1, 140.4, 146.8, 148.4, 163.3 (OCO), 116.0 (=CHCl), 40.2 (CH ₂ Cl)
21	166.6	103.7		(119.7, 132.3, 132.4, 133.0, 133.3, 134.9, 135.7) ^f							119.7	32.4	141.1, 141.8, 151.0, 152.8 (C-3a, 5, 10, 12a), 187.1 (CO), 49.4 (CH ₂ Cl)
14	173.3	— ^d	— ^d	143.1	142.8	145.2	137.7	— ^d	154.6	143.3	129.0	33.1	122.4, 144.6, 150.8, 151.4
15	173.9	38.6	155.1	— ^d	141.1	143.4 ^e	143.9 ^e	141.0	— ^d	159.2	125.9	34.5	138.2, 144.3, 146.1, 164.8

^a 400 MHz, δ /ppm in CDCl₃. ^b 125 MHz, δ /ppm in CDCl₃. ^c The signals of unassigned carbons and quaternary carbons, or side-chain carbons for **19**, **20** and **21** are listed. ^d The signals are not distinctly assigned. ^e Reversed assignment of the signals at δ 126.7 and 127.0 is also possible. ^f The carbon signals of C-4, -6, -7, -8, -9, -11 and -12.

**Scheme 4** Reagents and conditions: i, **5**, CH₂Cl₂, 0 °C; ii, **6**, ClCH₂CH₂Cl, reflux

reaction of chloroketene with **6** under reflux in 1,2-dichloroethane, on the other hand, afforded only **21** in low yield (Scheme 4) (Table 1, entry 4). The reactivity of chloroketene toward **6** is also low as for dichloroketene. The formation of compound **21** from compound **6** can be explained similarly to the production of **19** from **5**. The expected acetylated product of **21** was not isolated.

The structures of compounds **19**, **20** and **21** were easily deduced on the basis of elemental analyses and ^1H and ^{13}C NMR (Table 3) spectral data, as well as by the comparison of their spectral data with those of compounds **4a**, **b**, **7b** and **11a**, **b**.

In conclusion, the cycloaddition of chlorinated ketenes with methano[11]annulenes **5** and **6** were investigated and gave the expected 2*H*-methanocycloundeca[*b*]furan-2-one ring systems. The spectroscopic properties of these ring systems seem to be similar to those of 2*H*-cyclohepta[*b*]furan-2-one. Studies concerning the reactivities and synthetic applications of 2*H*-methanocycloundeca[*b*]furan-2-ones are now underway.¹⁶

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. UV spectra were measured on a Shimadzu UV-3101PC spectrometer. Mass spectral studies were conducted by using a Shimadzu GCMS QP-1000 spectrometer. Unless otherwise specified, ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{17}O NMR (54 MHz) spectra were recorded in CDCl₃ on a JNM-

GSX400 spectrometer and the chemical shifts are given relative to internal SiMe₄ for ^1H , ^{13}C , and external D₂O for ^{17}O , respectively. *J* Values are given in Hz. Microanalyses were performed at the Material Characterization Central Laboratory of Waseda University. M.p.s were recorded on a Büchi apparatus and are uncorrected. All the reactions were performed under a dry nitrogen atmosphere.

Cycloaddition of Dichloroketene with 3,8-Methano[11]annulene 5.—To a stirred solution of methanoannulene **5** (3.79 g, 22.3 mmol) and triethylamine (9.01 g, 89.2 mmol) in CH₂Cl₂ (100 cm³) was added dichloroacetyl chloride (6.55 g, 44.6 mmol) in CH₂Cl₂ (50 cm³) dropwise over 20 min at 0 °C. After the addition was completed, the mixture was stirred for a further 10 min at 0 °C and then aqueous NH₄Cl solution was added. The reaction mixture was extracted with CH₂Cl₂ and the extract was dried over Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was crystallized from methanol to give 3-chloro-2*H*-4,9-methanocycloundeca[*b*]furan-2-one **4a** (4.56 g, 84%). The mother liquor was then chromatographed on silica gel to give a mixture of 3-chloro-2*H*-4,9-methano- **4a** and 3-chloro-2*H*-6,11-methanocycloundeca[*b*]furan-2-one **7a** (58:42) (517 mg, 9%).

For **4a**: dark red prisms; m.p. 168–169 °C (from EtOH); δ_{H} 0.80 (1 H, d, *J* 11.7, 13-H_b), 2.40 (1 H, dt, *J* 11.7, 1.5, 13-H_a), 6.31 (1 H, dd, *J* 11.2, 10.8, 11-H), 6.80 (1 H, d, *J* 10.8, 12-H), 6.87–6.91 (1 H, m, 8-H), 7.14 (1 H, d, *J* 11.2, 10-H), 7.28–7.30 (2 H, m, 6-, 7-H) and 7.51–7.55 (1 H, m, 5-H); λ_{max} (hexane)/nm (log ϵ /dm³

$\text{mol}^{-1} \text{cm}^{-1}$) 424 (4.11); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1743; m/z (rel. intensity) 244 (M^+ , 75%) and 153 (100) (Found: C, 68.4; H, 3.5. $\text{C}_{14}\text{H}_9\text{ClO}_2$ requires C, 68.72; H, 3.71%).

Cycloaddition of Dichloroketene with 4,9-Methano[11]annulenone 6.—To a stirred solution of methanoannulenone **6** (500 mg, 2.94 mmol) and triethylamine (5.94 g, 58.8 mmol) in CH_2Cl_2 (30 cm^3) was added dichloroacetyl chloride (3.47 g, 23.5 mmol) in CH_2Cl_2 (25 cm^3) dropwise over 3 h under reflux. The reaction mixture was refluxed for a further 1 h and then aqueous NH_4Cl was added. The mixture was extracted with CH_2Cl_2 and the extract was washed with aqueous NaHCO_3 , and dried over Na_2SO_4 . The solvent was removed and the residue was separated by TLC (CH_2Cl_2 –hexane, 5:1) to give unchanged **6** (60 mg, 12%) and dark red crystals, which were further purified by TLC (hexane–AcOEt, 2:1) to give 3-chloro-2H-5,10-methanocycloundeca[b]furan-2-one **11a** (180 mg, 25%).

For **11a**: dark red prisms; m.p. 161–163 °C (from EtOH); δ_{H} 1.95 (1 H, dt, J 10.9, 1.8, 13- H_a), 2.11 (1 H, d, J 10.9, 13- H_b), 6.53–6.61 (2 H, m, 7-, 8-H), 6.65 (1 H, dd, J 7.8, 1.2, 11-H), 6.95 (1 H, s, 4-H), 7.04 (1 H, d, J 10.2, 9-H), 7.07 (1 H, d, J 7.8, 12-H) and 7.11 (1 H, d, J 10.1, 6-H); $\lambda_{\text{max}}(\text{hexane})/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 428 (4.02); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1745; m/z (rel. intensity) 244 (M^+ , 61%) and 153 (100) (Found: C, 68.3; H, 3.6. $\text{C}_{14}\text{H}_9\text{ClO}_2$ requires C, 68.72; H, 3.71%).

General Procedure for the Dechlorination of 4a, a Mixture of 4a and 7a, 11a or 1a.—A solution of 3-chloro-2H-methanocycloundeca[b]furan-2-one **4a**, **7a** or **11a** (1 mmol) or 3-chloro-2H-cyclohepta[b]furan-2-one **1a** (1 mmol) and NaI (5 mmol) in $\text{CF}_3\text{CO}_2\text{H}$ (2 cm^3) was stirred for the time indicated in Table 2. The reaction mixture was then poured into aqueous NaHCO_3 , extracted with CH_2Cl_2 , and the extract was dried over Na_2SO_4 . The solvent was evaporated and then the residue was purified by TLC on silica gel (CH_2Cl_2) to give the product. The results are summarized in Table 2.

For 2H-4,9-methanocycloundeca[b]furan-2-one **4b**: reddish purple prisms; m.p. 118–119 °C (from MeOH); δ_{H} 0.80 (1 H, d, J 11.7, 13- H_b), 2.48 (1 H, d, J 11.7, 13- H_a), 6.28 (1 H, dd, J 12.1, 11.0, 11-H), 6.39 (1 H, d, J 1.5, 3-H), 6.76 (1 H, dd, J 11.0, 1.5, 12-H), 6.84 (1 H, d, J 6.2, 8-H), 7.06 (1 H, d, J 12.1, 10-H), 7.12 (1 H, d, J 6.2, 5-H), 7.18 (1 H, dd, J 10.6, 6.2, 6-H) and 7.23 (1 H, dd, J 10.6, 6.2, 7-H); δ_{O} 237 (O-1) and 327 (C=O); $\lambda_{\text{max}}(\text{hexane})/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 418 (4.08); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1732; m/z (rel. intensity) 210 (M^+ , 33%) and 153 (100) (Found: C, 79.8; H, 4.6. $\text{C}_{14}\text{H}_{10}\text{O}_2$ requires C, 79.99; H, 4.79%).

For 2H-6,11-methanocycloundeca[b]furan-2-one **7b**: red needles; m.p. 133–134 °C (from MeOH); δ_{H} 0.74 (1 H, d, J 11.3, 13- H_b), 2.29 (1 H, dt, J 11.3, 1.4, 13- H_a), 6.14 (1 H, d, J 10.7, 3-H), 6.72 (1 H, d, J 12.1, 4-H), 6.80–6.85 (1 H, m, 7- or 10-H), 6.89–6.94 (1 H, m, 7- or 10-H), 7.18 (1 H, d, J 12.1, 5-H), 7.22–7.25 (2 H, m, 8-, 9-H) and 7.36 (1 H, s, 12-H); $\lambda_{\text{max}}(\text{hexane})/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 411 (4.04); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1731; m/z (rel. intensity) 210 (M^+ , 100%) (Found: C, 79.9; H, 4.7. $\text{C}_{14}\text{H}_{10}\text{O}_2$ requires C, 79.99; H, 4.79%).

For 2H-5,10-methanocycloundeca[b]furan-2-one **11b**: dark red prisms; 117–118 °C (from MeOH); δ_{H} 1.95 (1 H, dt, J 10.8, 1.7, 13- H_b), 2.00 (1 H, d, J 10.8, 13- H_a), 5.98 (1 H, dd, J 11.4, 1.0, 3-H), 6.52 (1 H, ddd, J 11.4, 5.7, 1.7, 8-H), 6.54 (1 H, ddd, J 11.4, 5.7, 1.3, 7-H), 6.63 (1 H, dd, J 7.7, 1.3, 11-H), 6.95 (1 H, dm, J 11.4, 6-H), 7.00 (1 H, s, 4-H), 7.04 (1 H, d, J 7.7, 12-H) and 7.10 (1 H, dm, J 11.4, 9-H); $\lambda_{\text{max}}(\text{hexane})/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 435 (3.96); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1732; m/z 210 (M^+ , 100%) (Found: C, 79.9; H, 4.7. $\text{C}_{14}\text{H}_{10}\text{O}_2$ requires C, 79.99; H, 4.79%).

For 2H-cyclohepta[b]furan-2-one **1b**: δ_{H} 5.78 (1 H, d, J 1.1,

3-H), 6.83 (1 H, dd, J 10.3, 8.4, 6-H), 6.97 (1 H, J 8.8, 1.5, 8-H), 7.01 (1 H, d, J 10.3, 8.8, 7-H), 7.04 (1 H, dd, J 11.4, 8.4, 5-H) and 7.30 (1 H, d, J 11.4, 4-H).

Cycloaddition of 3,8-Methano[11]annulenone 5 with Chloroketene.—To a stirred solution of methanoannulenone **5** (41 mg, 0.24 mmol) and triethylamine (365 mg, 3.6 mmol) in CH_2Cl_2 (2 cm^3) was added chloroacetyl chloride (245 mg, 2.16 mmol) in CH_2Cl_2 (1 cm^3) dropwise over 10 min at 0 °C. The mixture was stirred for a further 3 h and then extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4 . The solvent was removed under reduced pressure and then the residue was separated by TLC on silica gel (benzene–AcOEt, 10:1) to give 3-unsubstituted-**4b** (7 mg, 14%), 3-chloroacetyl-**19** (7 mg, 10%) and 3-{(2-chloro-1-chloroacetoxy)vinyl}-2H-4,9-methanocycloundeca[b]furan-2-one **20** (35 mg, 40%).

For **19**: dark red prisms; m.p. 192–193 °C (from EtOH); δ_{H} 0.12 (1 H, d, J 12.1, 13- H_b), 0.82 (1 H, d, J 12.1, 13- H_a), 5.00 and 5.02 (1 H each, 2 \times d, J 16.5, CH_2Cl), 7.00 (1 H, dd, J 11.4, 11.0, 11-H), 7.51 (1 H, d, J 6.6, 8-H), 7.62 (1 H, d, J 11.4, 12-H), 7.66–7.75 (2 H, m, 6-, 7-H), 7.81 (1 H, d, J 11.9, 10-H) and 8.86 (1 H, d, J 7.0, 5-H); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1736; m/z (rel. intensity) 286 (M^+ , 58%) and 237 (100) (Found: C, 67.2; H, 4.0. $\text{C}_{16}\text{H}_{11}\text{ClO}_3$ requires C, 67.03; H, 3.87%).

For **20**: dark red prisms; m.p. 138–139 °C (from EtOH); δ_{H} 0.88 (1 H, d, J 12.5, 13- H_b), 2.25 (1 H, d, J 12.5, 13- H_a), 4.16 and 4.21 (1 H each, 2 \times d, J 15.4, CH_2Cl), 6.35 (1 H, dd, J 11.7, 11.0, 11-H), 6.87 (1 H, d, J 11.0, 12-H), 6.91 (1 H, d, J 6.2, 8-H), 7.14 (1 H, d, J 6.6, 5-H), 7.17 (1 H, d, J 11.7, 10-H), 7.18 (1 H, s, =CHCl), 7.22 (1 H, dd, J 10.6, 6.6, 6-H) and 7.28 (1 H, dd, J 10.6, 6.2, 7-H); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1738; m/z (rel. intensity) 362 (M^+ , 28%) and 165 (100) (Found: C, 59.3; H, 3.3. $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{O}_4$ requires C, 59.53; H, 3.33%).

Cycloaddition of 4,9-Methano[11]annulenone 6 with Chloroketene.—To a stirred solution of annulenone **6** (100 mg, 0.58 mmol) and triethylamine (1.07 g, 10.4 mmol) in 1,2-dichloroethane (5 cm^3) was added chloroacetyl chloride (400 mg, 3.48 mmol) in 1,2-dichloroethane (5 cm^3) dropwise over 10 min under reflux. The mixture was refluxed for a further 7 h and then the solvent was evaporated and the residue was chromatographed on alumina. The fractions eluted with hexane–AcOEt (1:1) were further separated by TLC on silica gel (hexane–AcOEt, 2:1) to give unchanged **6** (22 mg, 22%) and 3-chloroacetyl-2H-5,10-methanocycloundeca[b]furan-2-one **21** (16 mg, 9%).

For **21**: dark red prisms; m.p. 205 °C (decomp.) (from EtOH); δ_{H} 0.00 (1 H, dd, J 10.6, 1.8, 13- H_b), 0.96 (1 H, d, J 10.6, 13- H_a), 4.93 and 4.96 (1 H each, 2 \times d, J 16.1, CH_2Cl), 7.23–7.28 (2 H, m, 7-, 8-H), 7.55 (1 H, d, J 8.8, 11-H), 7.69–7.75 (2 H, m, 6-, 9-H), 7.88 (1 H, d, J 8.8, 12-H) and 9.06 (1 H, s, 4-H); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1738; m/z (rel. intensity) 286 (M^+ , 43%) and 237 (100) (Found: C, 66.9; H, 3.9. $\text{C}_{16}\text{H}_{11}\text{ClO}_3$ requires C, 67.03; H, 3.87%).

Reaction of Chloroketene with 2H-4,9-Methanocycloundeca[b]furan-2-one 4b.—To a stirred solution of annulenone **4b** (30 mg, 0.14 mmol) and triethylamine (43 mg, 1.71 mmol) in CH_2Cl_2 (2 cm^3) was added chloroacetyl chloride (97 mg, 0.86 mmol) in CH_2Cl_2 (1 cm^3) dropwise at room temperature. The reaction mixture was stirred for 1 day at room temperature and then the mixture was extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4 . The solvent was evaporated and then the residue was purified by TLC on silica gel (benzene–AcOEt, 10:1) to give unchanged **4b** (30 mg, 100%).

Reaction of Chloroacetyl Chloride with 2H-4,9-Methanocycloundeca[b]furan-2-one 4b.—A solution of annulenone **4b** (10 mg, 0.05 mmol), chloroacetyl chloride (54 mg, 0.48 mmol),

and pyridine (38 mg, 0.5 mmol) in CH_2Cl_2 (1.5 cm^3) was stirred at room temperature for 1 day. The reaction mixture was then extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4 . The solvent was evaporated and then the residue was purified by TLC on silica gel (benzene–AcOEt, 10:1) to give unchanged **4b** (8 mg, 80%).

X-Ray Crystallographic Analysis of 3-Chloro-2H-4,9-Methanocycloundeca[b]furan-2-one 4a.—Dark red crystals, $\text{C}_{14}\text{H}_9\text{O}_2\text{Cl}$ monoclinic space group $P2_1/n$, $a = 10.187(1)$, $b = 7.804(1)$, $c = 13.946(1)$ Å, $\beta = 90.531(7)^\circ$, $V = 1108.5(2)$ Å³. The unit cell contained four molecules giving a calculated density of 1.47 g cm^{-3} . A total of 2599 reflections with $2\theta = 53^\circ$ were collected on an ENRAF–NONIUS CAD4 diffractometer with a rotating anode (5 mA, 20 kV) using graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.710$ 69 Å) with $2\theta-\omega$. The structure was solved by the direct method and refined by the block-diagonal least-squares method anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms which were located by a D-Fourier map. The final R -factor was 0.037 for 1244 unique reflections with $F_o > 3\sigma(F_o)$. All calculations were carried out on a DEC computer using the applied library program Molten. Tables of atomic coordinates, bond lengths and angles, and thermal parameters for **4a** have been deposited at the Cambridge Crystallographic Data Centre.*

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

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