

## CYCLOADDITIONS OF DICHLOROKETENE TO OLEFINS AND DIENES<sup>1, 2</sup>

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**Abstract**—Dichloroketene, as obtained *in situ* by dehydrohalogenation of dichloroacetyl chloride with triethylamine or zinc dehalogenation of trichloroacetyl bromide, is a reactive and unstable molecule. It reacts very readily with conjugated dienes to give exclusively derivatives of  $\alpha,\alpha$  dichlorocyclobutanone. No 1,4-cycloadducts were detected. Other activated olefins such as indene or dihydropyran also give good yields of cycloadducts. Electrophilic olefins such as methyl methacrylate or methyl fumarate are completely inert toward dichloroketene. Unlike less reactive ketenes, dichloroketene reacts readily even at room temperature with such unactivated olefins as cyclopentene and cyclohexene. However such bicyclic olefins as norbornene or norbornadiene are shown to be poor ketenophiles. These results point to a concerted cycloaddition involving an orthogonal approach of the ketene and olefin in accordance with Woodward and Hoffmann's suggestion. The scope and synthetic utility of these cycloadditions are discussed.

**Résumé**—Le dichlorocétène obtenu *in situ* par déshydrohalogénéation du chlorure de dichloracétyle par la triéthylamine ou par déshalogénéation du bromure de trichloracétyle au zinc est une molécule instable et très réactive. Il réagit très facilement avec les diènes conjugués pour fournir exclusivement des dérivés de l' $\alpha,\alpha$  dichlorocyclobutanone. Aucun adduit 1,4 n'a pu être mis en évidence. D'autres oléfines activées telles que l'indène ou le dihydropyrane s'additionnent au dichlorocétène avec de bons rendements. Par contre les oléfines électrophiles ne réagissent pas du tout. Contrairement aux autres cétènes moins réactifs, le dichlorocétène réagit facilement même à température ordinaire avec des oléfines non activées comme le cyclopentène ou le cyclohexène. Toutefois des oléfines bicycliques comme le norbornène ou le norbornadiène sont des céténophiles peu réactifs. Les résultats obtenus suggèrent un mécanisme concerté dans lequel les réactifs s'approchent de manière orthogonale en accord avec la suggestion faite par Woodward et Hoffmann. On discute le champ d'application et l'utilité de ces réactions pour la synthèse organique.

### I. INTRODUCTION

WHILE ketene and its alkyl- and aryl derivatives have been extensively studied,<sup>3</sup> haloketenes have received comparatively little attention. Staudinger<sup>4</sup> described dichloroketene and some alkylchloro- and bromoketenes as unstable compounds which polymerise readily even at very low temperatures. More recently the preparation of stable dilute solutions of dichloro- and dibromoketene has been claimed;<sup>5</sup> however the evidence for their existence is inconclusive. § Similarly a claim for the preparation of an ether solution of difluoroketene has been disproven<sup>7</sup>: instead

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§ The presence of a weak absorption band at  $1940\text{ cm}^{-1}$  does not reasonably demonstrate the presence of dichloroketene. Since ketene itself absorbs at  $2160\text{ cm}^{-1}$ , this would mean that the substitution of two H atoms for two Cl atoms considerably lowers the asymmetric stretching frequency. Furthermore the IR spectrum of the "ketene" solution exhibits strong bands around  $1800\text{ cm}^{-1}$  which can be assigned to dichloroketene dimers.<sup>6</sup>

difluoroketene appears as a short-lived intermediate which can be trapped at lower temperatures with benzaldehyde or acetone to yield  $\beta$ -lactones.<sup>8</sup>

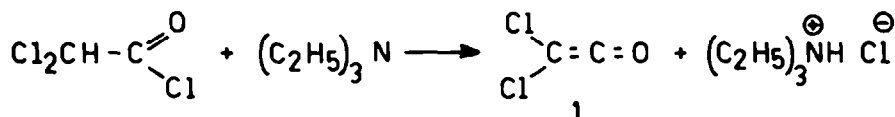
Haloketenes are expected to be more electrophilic due to the electronegativity effect of the halogen substituents. Furthermore the ability of chlorine or bromine to stabilize a negative charge on the  $\alpha$  C atom is expected to increase the tendency of these haloketenes to undergo nucleophilic additions. This suggested to us in 1966 that dichloroketene could be much more reactive than ketene in cycloaddition reactions to nucleophilic multiple bonds. This possibility was especially attractive from the standpoint of the synthetic chemist since it would offer a simple route toward functionally substituted 4-membered rings. These expectations were first realized when it was found that dichloroketene cycloadded readily to cyclopentadiene and cyclopentene. After these preliminary reports<sup>2a, 9</sup> several papers from this<sup>2b, 10</sup> and other laboratories<sup>11</sup> confirmed the synthetic usefulness of dichloroketene and other reactive haloketenes.

We now report in detail the cycloaddition of dichloroketene to olefins and dienes as well as some transformations of the dichlorocyclobutanones which were obtained.

## II RESULTS

### A. Cyclopentadiene

The dehydrochlorination of dichloroacetylchloride with triethylamine is a convenient method for preparing dichloroketene **1** *in situ*.

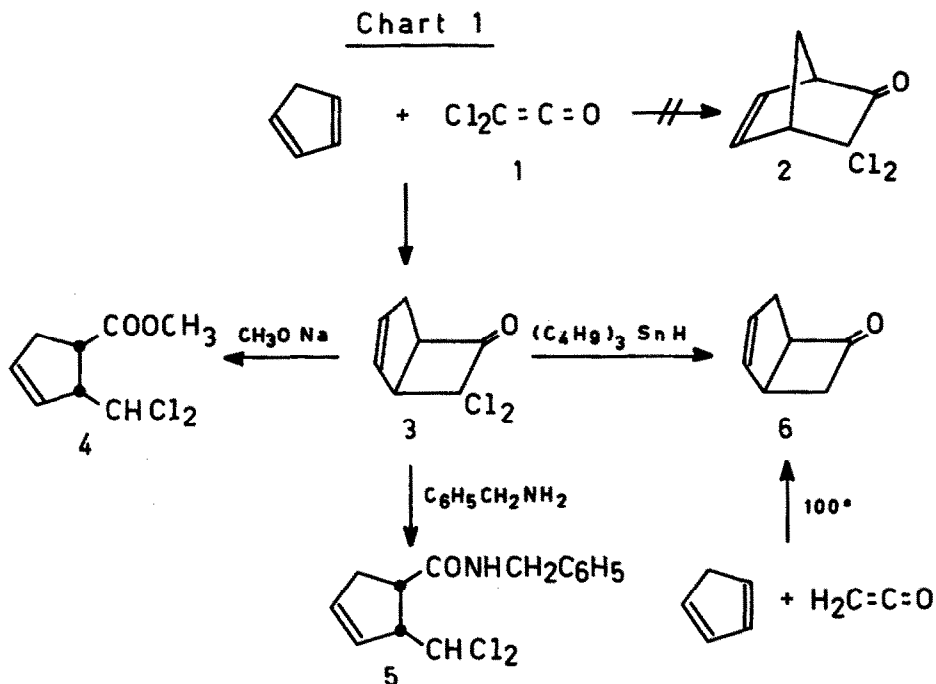


In the presence of a 3-fold excess of cyclopentadiene the dehydrochlorination yielded the triethylamine salt (> 90%) and a 1 : 1 dichloroketene-cyclopentadiene adduct (Chart 1) which was homogeneous to vapour phase and TLC under a variety of experimental conditions. The IR spectrum of the adduct showed a strong CO absorption at 1807  $\text{cm}^{-1}$  (indicative of a cyclobutanone bearing two electronegative  $\alpha$ -substituents) and a double bond stretching absorption at 1608  $\text{cm}^{-1}$ . The PMR spectrum exhibited three signal groupings in the ratio 1 : 1 : 1 (Table 1) centered respectively at 5.93, 4.15, and 3.72 ppm. These spectral data readily excluded the bicyclic structure **2** resulting from a Diels-Alder cycloaddition but were fully consistent with a cyclobutanone structure such as **3**.

However it remained to establish the position of the double bond. The reaction of **3** with sodium methoxide in methanol between  $-15^\circ$  and  $0^\circ$  gave a 73% yield of **4** which was found to be homogeneous by thin-layer and vapor-phase chromatographic analyses. Its IR spectrum showed absorptions at 1739  $\text{cm}^{-1}$  and 1620  $\text{cm}^{-1}$ .

The proton magnetic resonance spectrum showed three signal groupings: the first grouping (3 H) centered around 5.80 ppm consisted of a doublet (5.85  $\delta$ ,  $J=4$  Hz) corresponding to the  $-\text{CHCl}_2$  grouping and a multiplet due to two olefinic protons; the characteristic signal of the OMe-group appeared at 3.71 ppm superimposed on a multiplet due to the tertiary allylic proton; the three remaining protons gave rise to a broad multiplet around 3.1 ppm. No change occurred in the  $\text{C}=\text{O}$  stretching frequency and in the NMR signal corresponding to the olefinic protons after prolonged heating of **4** in refluxing methanol containing catalytic amounts of sodium methoxide or hydrogen chloride. This behaviour supports structure **4** with a double bond in  $\gamma, \delta$  position with

respect to the ester group since, under these conditions, the isomer with a double bond in the  $\beta,\gamma$  position would be expected to isomerise to the more stable  $\alpha,\beta$  conjugated ester.



Other nucleophilic reagents such as benzylamine reacted instantaneously at room temperature with 3 to yield quantitatively the corresponding amides 5.† Furthermore dechlorination of the adduct with excess tributyltinhydride or with zinc in acetic acid<sup>13</sup> yielded the parent ketone 6 which had been previously obtained in low yield from ketene and cyclopentadiene at  $100^\circ$ .<sup>14</sup> In order to ensure that no unstable adduct could have escaped detection in the analytical investigation, the crude cycloaddition mixture was directly dechlorinated and the resulting products which had a higher thermal stability were investigated by analytic and preparative glpc. From these experiments it could safely be concluded that 3 was indeed the single cycloaddition product.

The scope of the reaction has not been fully investigated with respect to applicable unsaturated structures and reaction conditions; however a synthesis has been devised which gives reproducible yields of cyclobutanones from dichloroketene and some representative olefinic compounds. In general the best yields were obtained when the dehydrochlorination of dichloroacetylchloride with triethylamine was conducted between  $30^\circ$  and  $50^\circ$  in a hydrocarbon solvent containing an excess of the ketenophile.

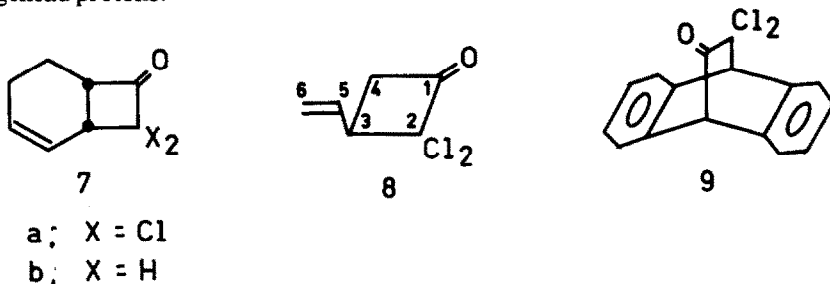


†  $\alpha\alpha'$  Debromocyclobutanones had been shown previously to undergo a similar ring opening under the influence of nucleophiles<sup>12</sup>

The dehalogenation of trichloroacetyl bromide,<sup>5a</sup> another way of preparing dichloroketene *in situ*, usually gave lower yields and less reproducible results.

### B. Other dienes

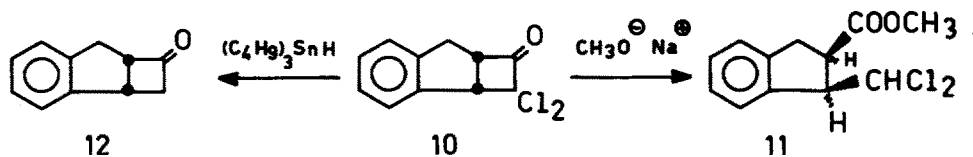
Cyclohexadiene gave a single cycloadduct **7a** which showed IR absorptions at 1810 and 1649  $\text{cm}^{-1}$ . It was dechlorinated with tributyltinhydride to the known bicyclo [4.2.0] oct-2-en-7-one **7b**.<sup>15</sup> The *cis*-configuration at the ring junction was confirmed by double resonance studies which showed a coupling constant of 10 Hz between the two bridgehead protons.



A linear diene such as 1,3 *butadienen* reacted more sluggishly to give an adduct **8** which was purified by preparative gas chromatography. The IR spectrum displayed a CO stretching absorption at 1805  $\text{cm}^{-1}$  together with peaks at 3015, 1640, 980 and 930  $\text{cm}^{-1}$  indicative of vinyl group. The vinyl proton appeared as two multiplets at 5.36  $\delta$  (2H-6) and 6.02  $\delta$  (H-5,  $J_{3,5} = 3.6$  Hz,  $J_{3,6 \text{ cis}} = 10$  Hz,  $J_{3,6 \text{ trans}} = 16$  Hz), respectively. As expected anthracene was recovered quantitatively when exposed to dichloroketene. No traces of the 1,4 cycloadduct **9** could be detected.

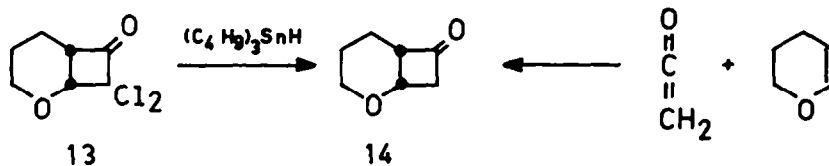
### C. Activated olefins

Indene gave a solid adduct **10**, m.p. 78–78.5°, in 41% yield. The spectral data are in agreement with those reported by previous workers.<sup>16</sup> However the spectral data were of no help in proving the direction of cycloaddition.



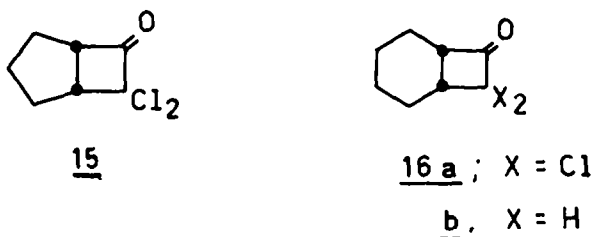
This was done by opening the 4-membered ring by treatment with methanolic sodium methoxide at  $-15^\circ$ . The single product (94%) showed spectral data in agreement with **11**; this structure was further supported by double resonance studies which confirmed spin-spin coupling of proton H-3 to H-4 ( $J = 5$  Hz) and to H-6 ( $J = 3$  Hz). The same conclusion was reached independently by Poots and Harmon<sup>17</sup> after the completion of this work. Dechlorination with tributyltinhydride in refluxing cyclohexane yielded 7-*H*-cyclobut[*a*]inden-1-one **12**.

Dihydropyran gave a solid adduct **13** which could be dechlorinated to the known 2-oxabicyclo[4.2.0]octan-7-one **14** previously obtained from ketene and dihydropyran.<sup>18</sup> As expected the electron-poor double bonds of methylmethacrylate or methylfumarate were completely inert toward dichloroketene.



#### D. Cyclopentene and cyclohexene

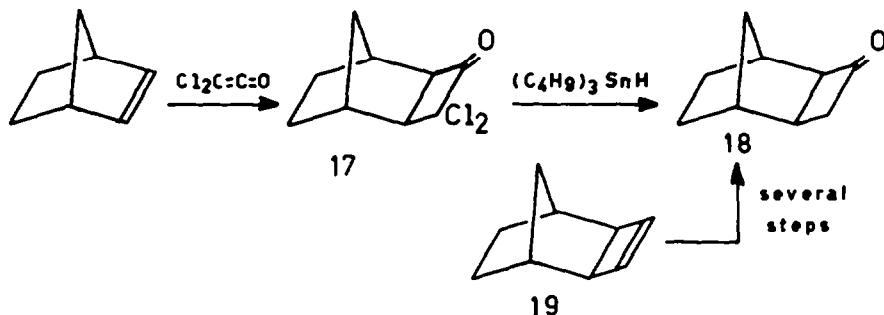
The dehydrochlorination of dichloroacetylchloride with triethylamine in the presence of unactivated olefins such as cyclopentene or cyclohexene gave cycloadducts **15** and **16a** in good yields (68 and 53% respectively). Both adducts showed the characteristic IR absorption around  $1800\text{ cm}^{-1}$ .



This behaviour of dichloroketene contrasts strongly with the relative inertness of ketene, alkyl- or even aryl-substituted ketene under the same experimental conditions.<sup>19</sup>

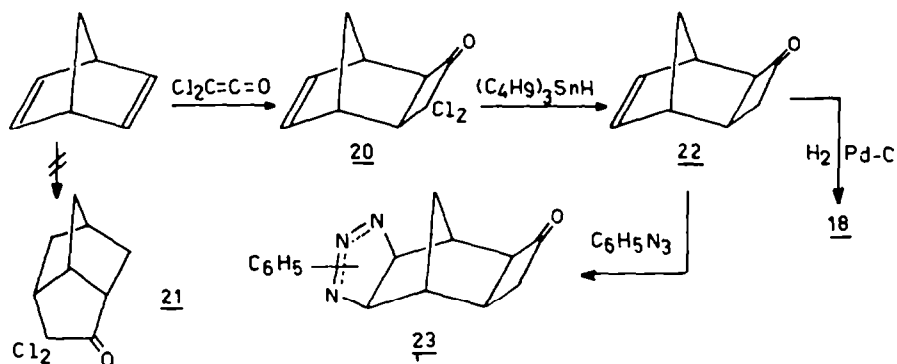
#### E. Strained olefins

The angle-strained double bond of bicyclo[2.2.1]hept-2-ene derivatives shows a high dipolarophilic reactivity.<sup>20</sup> Surprisingly norbornene and norbornadiene reacted only sluggishly with dichloroketene. Norbornene yielded a product (10%) in about 83% purity to which structure **17** was assigned (Chart 2). Dechlorination with tributyltinhydride gave a ketone whose spectral data were identical with exo-tricyclo[4.2.1.0<sup>2,5</sup>]nonan-3-one **18** previously obtained<sup>21</sup> from **19**.



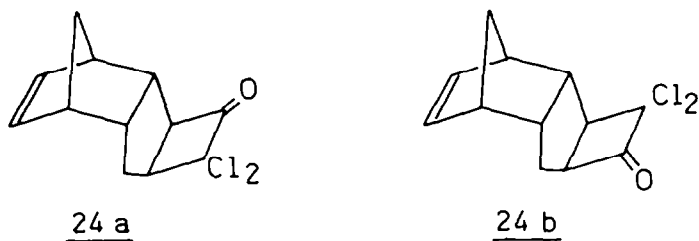
The reaction mixture obtained from the reaction of norbornadiene and dichloroketene was shown to contain the single (2 + 2)  $\pi$  cycloadduct **20** (22%, IR peaks at  $1804$  and  $1564\text{ cm}^{-1}$ , 2 olefinic protons at  $6.27\delta$ ) without any traces of the product **21** resulting from the addition across the homoconjugated system of double bond (Chart 3). The 4-membered ring was assigned the exo-configuration on the basis of the small value of the coupling constant between the bridgehead protons ( $J_{1,2} = 1.5\text{ Hz}$  and  $J_{5,6} = 1\text{ Hz}$ ).<sup>22</sup>

Chart 3



Moreover dechlorination of 20 gave the unsaturated ketone 22 ( $\nu_{\text{C}=\text{O}}$   $1778\text{ cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}}$   $1569\text{ cm}^{-1}$ ) which reacted readily with phenylazide to yield the isomeric adducts 23. Catalytic hydrogenation of 22 gave 18. Stereoelectronic factors and relief of torsional strain between the bonds at C—1 and C—2 are probably responsible for the exclusive formation of the exo-adducts, the latter effect being particularly important in a multicentered transition state since it would be simultaneously operative at two centers.

The poor ketenophilic reactivity of the strained double bond of the bicyclo[2.2.1]heptene system is dramatically demonstrated by the behaviour of dicyclopentadiene toward dichloroketene. When dichloroketene was generated in a fourfold excess of dicyclopentadiene, the only detectable product obtained in 58% yield was shown to result from the attack of the ketene on the 5-membered ring double bond: an examination of the NMR spectrum of the crude mixture after removal of excess dicyclopentadiene showed the disappearance of the higher field olefinic protons corresponding to the cyclopentene double bond (around  $5.5\delta$ ), whereas the other two olefinic hydrogens which are somewhat more deshielded ( $6.2\delta$ ) were still present. No effort was made to distinguish between 24a or 24b.



### III DISCUSSION

#### Reactivity

In spite of a high tendency to polymerize, dichloroketene enters readily in cycloaddition reactions with olefins or dienes. A rough qualitative comparison of the behaviour of various ketenes toward cyclopentene leads to the following reactivity sequence:

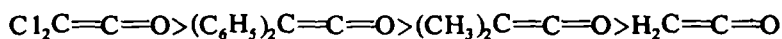


TABLE I. NMR SPECTRAL DATA<sup>a</sup>



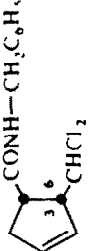


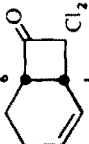




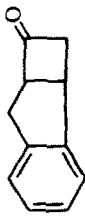

No.	Compound	Assignments, type of hydrogen			
		Olefinic, aromatic	Alkyl	Tertiary cyclic	Secondary cyclic
3		5.93 m (2)		4.15 m (1.97)	2.72 m (2.03)
4		5.85 m (2 + 1, overlapping) $J_{3,6} = 4$	3.7 s, m (3 + 1, overlapping)	2.90 broad (1 + 2, overlapping)	
5		7.33 s (5.14)	6.36 d (1.08) $J_{3,6} = 6.5$ 4.45 d (2) $J^c = 6$	3.65 m (1)	2.63 m (1.95)
6		5.96 m (2 + NH, overlapping)		3.17 m (1)	
		5.82 m (1.96)		3.82 m (1.01)	3.07 m (1) $J_{5,7_{exo}} = 2.5$ $J_{1,7_{exo}} = 8.5$ 2.71 m (3.04)
6-d <sub>2</sub> <sup>b</sup>		5.82 m (2)		3.48 m (1)	2.55 m (2)
7a		5.97 m (2.05)		3.82 m (1) 3.48 m (1)	2.00 broad (4.07)


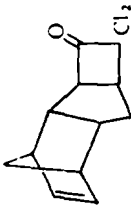
TABLE 1 (continued) NMR SPECTRAL DATA

No.	Compound	Assignments, type of hydrogen			
		Olefinic, aromatic	Alkyl	Tertiary cyclic	Secondary cyclic
7b		5.88 m (1.93)		3.20 m (2 + 1, overlapping) 2.47 ddd (1) $J_{1,8endo} \cong J_{6,8endo} \cong 2.3$ $J_{endo(8)} \cong 1.5$ 1.90 broad (3.87)	
8		6.02 ddd (1.04), $J_{5,6trans} = 16$ ; $J_{5,6cis} = 10$ ; $J_{3,5} = 6$ 5.40 d with additional 5.32 d fine splitting (2.08, overlapping)		3.38 m (1 + 2, overlapping)	
10		7.27 m (4.1)		4.42 m (1.99)	3.27 m (1.91)
11		7.27 m (4.04)	6.20 d (0.91) $J_{3,6} = 3$ 3.78 s (3, overlapping)	4.4 m (1.3) $J_{3,4^p} = 5$	3.37 m (1 + 2, overlapping)
12		7.17 s (3.9)			3.83 m (2, overlapping) 3.11 broad (4, overlapping)
13				4.37 d (0.9) $J_{1,6} = 5.5$ 3.65 broad (1 + 2)	1.65 broad (4.17)



<b>14</b>		4:38 ddd (0.94) $J_{1,8endo} = 1$ $J_{1,6} \cong J_{1,8exo} \cong 5.5$ 3:79 m (1.05)	3:25 broad (2.88) 2:57 dd (0.97) $J_{endo\theta} = 17$ 1:7 broad (4.16)
<b>15</b>		4:02 m (1) 3:39 m (1)	~2 broad (6)
<b>16a</b>		3:90 m (0.83) 2:93 m (0.93)	~1.7 broad (8.24)
<b>16b</b>		3:20 broad (2) 2:00 broad (10.07)	
<b>18</b>			3:02 m (1 + 1, overlapping) 2:54 m (3 + 1, overlapping) 1:42 broad (6.1)
<b>20</b>		6:27 dd (2.06) $J_{7,6} = J_{8,1} = 2$ $J_{7,9} = J_{8,9} = 1.4$	3:55 ddd (1.11) $J_{2,5} = 7; J_{2,1} = 1.5; J_{2,9} = 1.5$ 3:32 m (1.99) 2:88 ddd (0.85) $J_{5,2} = 7$ $J_{5,6} = 1; J_{5,9} = 1$
<b>22</b>		6:19 m (1.76)	3:02 m (3.20) 2:65 m (0.80) 1:50 m (2.16) 2:20 m (1 + 1, overlapping)

TABLE 1 (continued) NMR SPECTRAL DATA

No.	Compound	Assignments, type of hydrogen			
		Olefinic, aromatic	Alkyl	Tertiary cyclic	Secondary cyclic
22-d, <sup>d</sup>		6.19 m (2)		3 m (3) 2.22 m (1)	1.50 m (2)
24		6.20 m (2)		3.63 m (0.9) 3.05 broad (4.9)	1.78 broad (4.2)

<sup>a</sup> Spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride solution. Values are given in parts per million ( $\delta$  scale) relative to tetramethylsilane (TMS) as internal standard ( $\delta = 0.00$ ); s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants (J) are expressed in numbers in parentheses denote number of H atoms based on peak areas.

<sup>b</sup> Double resonance experiments.

<sup>c</sup> This coupling between the  $\text{CH}_2$  and NH protons disappeared when the sample was shaken with NaOD/D<sub>2</sub>O.

<sup>d</sup> Obtained by treatment with  $\text{K}_2\text{CO}_3$  in D<sub>2</sub>O at 60°.

The higher reactivity of dichloroketene can be readily accounted for on the basis of the interplay of two factors; (a) a higher ground state energy and an increased electrophilic character resulting from the introduction of electronegative substituents on the naturally electrophilic ketene functional group; (b) a better stabilisation of any intermediate (or transition state) bearing a negative charge or a free electron on the  $\alpha$  C atom, a consequence of introducing two substituents belonging to the second period. The interplay of these two factors also explains the increased reactivity of fluoro- and chloroallenes<sup>23</sup> or acetylenes<sup>24</sup> as compared with the unsubstituted molecules.

### *Scope and synthetic utility*

In ketenes both the C=C and C=O double bonds are able to take part in polar cycloaddition reactions but usually reaction products resulting from addition across the C=C double bond are isolated.<sup>3a,25</sup> Dichloroketene is no exception and its cycloadditions to olefins and dienes actually represent an exceedingly useful method of synthesis of 4-membered carbon rings. The following advantages may be cited:

- (a) The reagents are cheap and readily available.
- (b) The experimental conditions are mild.
- (c) The reaction has a rather general applicability and in most cases the yields are moderate to good. Furthermore, even in the least favourable cases, this direct method of building four-membered rings is probably superior to others involving several steps.
- (d) The reaction is directiospecific: in the adducts the most nucleophilic carbon of the olefin is always attached to the *sp* C atom of the ketene.
- (e) The reaction has been shown to be stereospecific,<sup>10a</sup> thus allowing the formation of 4-membered rings bearing substituents which are in the same configuration as in the original olefins.
- (f) The cycloaddition products, i.e. the  $\alpha,\alpha$ -dichlorocyclobutanones, offer interesting synthetic possibilities. They can be readily dechlorinated to the parent ketones or reduced to the corresponding cyclobutanols.<sup>26</sup> As shown for **3**, the 4-membered ring could readily be opened by nucleophiles. However, in other cases, the action of a nucleophile such as sodium methoxide induced a rearrangement to cyclopropane derivatives.<sup>12b</sup> The most interesting synthetic application to date has certainly been the conversion of **3** to tropolone in 65% yields by hydrolysis in aqueous acetic acid containing sodium acetate.<sup>9</sup> This transformation has been extended to the synthesis of various tropolone derivatives<sup>27</sup> and to a synthesis of tropone<sup>26a</sup> from the monochloroketene-cycloheptadiene adduct.

### *Mechanism*

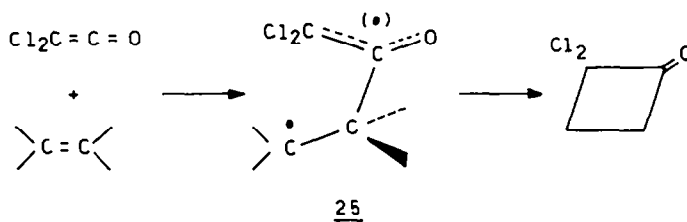
The main mechanistic problem is to find out whether the formation of the two new  $\sigma$  bonds occurs in a single stage or in a multi-step process.

If the  $\pi$  bonds break homolytically, the formation of the first  $\sigma$  bond leads to a 1,4-diradical **25** which closes to form the 4-membered ring (Chart 4).

The structure of our adducts can be readily rationalized in terms of the formation of the most stable diradical intermediates. The exclusive formation of 4-membered rings with conjugated dienes could be attributed to an entropic factor; however this argument is no longer valid for a diene constrained in a cisoid conformation where both 1,2 and 1,4 recombinations are almost equally probable: indeed, in a typical diradical reaction such as the cycloaddition of 1,1-dichloro-2,2-difluoroethylene to dienes or olefins, a *cis*-fixed

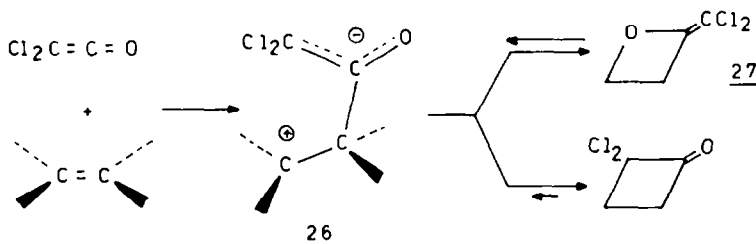
diene such as cyclopentadiene leads to a mixture of 1,2 and 1,4 cycloadducts whereas the "transoid" dienes gave only the 4-membered rings.<sup>28</sup> Moreover in the reaction of 1,1-dichloro-2,2-difluoroethylene with norbornadiene, Bartlett *et al.* found some addition across the homoconjugated system<sup>29</sup> in contrast to our observations in the analogous reaction of dichloroketene. Finally a diradical mechanism would not account readily

Chart 4



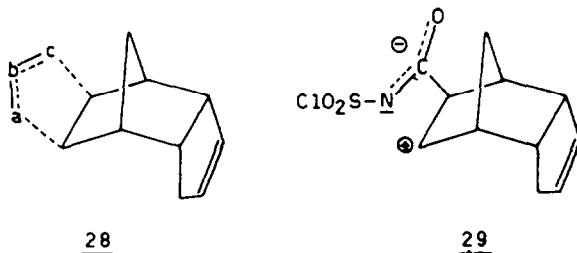
for the poor ketenophilic activity of electrophilic olefins. This observation however, as well as the directional specificity of the reaction, would be expected if the reaction started with a nucleophilic attack of the olefin onto the electrophilic central C atom of the ketenes leading to a 1,4-dipolar intermediate **26** (Chart 5).<sup>30</sup> The different modes of approach of the two reactants and their consequences on the nature and the stereochemistry of the products will be further discussed in a subsequent paper where stereochemical experiments will be presented.

Chart 5

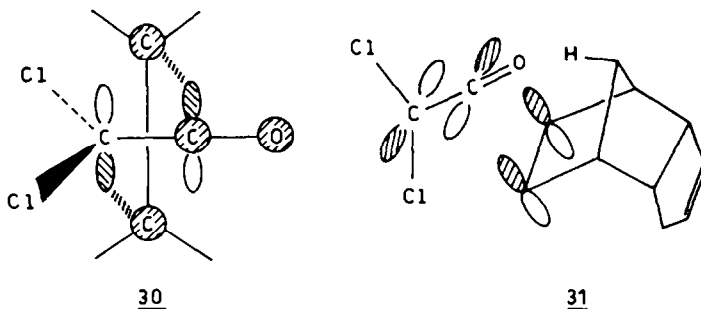


However it may be worth noting here that the ring closure leading from this 1,4-dipole to the cyclobutanone ring can occur only after a 90° rotation around the C—C bond of the ketene. Furthermore, since the recombination of the two ends of an ion pair is an exothermic process, it should have a transition state bearing more resemblance to the starting ion pair. Hence, since the electron density at the O atom must be greater than on the dichloromethyl group, one should expect the formation of some oxetane **27**. As a matter of fact oxetanes have been detected in the multi-step polar cycloaddition of *bis*-trifluoromethyl ketene with olefins.<sup>31</sup> However one must admit that the absence of oxetane in the products cannot be taken as a very strong argument against a multi-step mechanism since its formation is probably reversible and it may be unstable under the reaction conditions. The poor ketenophilic reactivity of the strained bicyclo [2.2.1] heptene system provides a rather strong argument against the two-step mechanisms. It is well-known that the energy-rich strained double bond of dicyclopentadiene shows a high dipolarophilic activity<sup>20</sup> and reacts much faster than the cyclopentene double bond in multi-step reactions such as the addition to *N*-chlorosulfonylisocyanate.<sup>32</sup> This

enhanced reactivity is undoubtedly due to the relief of strain accompanying either a concerted reaction leading to a 5-membered ring **28**, or the formation of a 1,4-dipole which cyclises to a 4-membered ring **29**. From these observations it follows that the exclusive addition of dichloroketene at the cyclopentene double bond of dicyclopentadiene cannot readily be reconciled with the formation of a dipolar intermediate.



A third mechanistic pathway suggested by Woodward and Hoffmann<sup>33</sup> has received some experimental support in recent times.<sup>34</sup> Ketenes considered as vinylidene ylides have a constitution which is ideal for playing the antarafacial role in a  $\pi 2_s + \pi 2_s$  cycloaddition. Such a process involves an orthogonal approach of the two molecules **30**, a situation which is favoured here by strong bonding interactions between the occupied  $\pi$  system of the olefin and the exceptionally low lying  $\pi^*_{C=O}$  level of the ketene. Such a mechanism accounts readily for the absence of 1,4 cycloadducts, for the directiospecificity, and for the higher reactivity of dichloroketene as compared to other ketenes.



Finally the geometry of the transition state accounts readily for the poor ketenophilic reactivity of the bicyclo [2.2.1] heptene system: in such a transition state there is only a very small relief of angle strain, if any; furthermore the orthogonal approach creates strong Pitzer interactions between the carbonyl oxygen and the *syn* hydrogen of the methylene bridge **31**.

#### IV EXPERIMENTAL

M.ps and b.ps are uncorrected. Microanalyses were performed by A. Bernhardt, Mülheim, Germany. IR spectra were measured, except where otherwise indicated, as liquid films on a Perkin-Elmer Model 21 or 257 spectrophotometer. Analytic and preparative GLPC separations were done with Aerograph instruments, Models 2-350 B, 204-1 B, and A-700 "Autoprep".

##### General procedures for cycloadditions

1. *Method A.* The reaction was conducted in a 3-necked round-bottomed flask fitted with a mechanical stirrer, a condenser, and a pressure-equalizing funnel. All solvents were dried and distilled before use. Tri-

ethylamine was refluxed over KOH pellets and distilled. In most experiments triethylamine was added dropwise into an hydrocarbon soln of the freshly distilled acid chloride and an excess of the diene or olefin. The reaction was exothermic and precipitation of the triethylamine hydrochloride was instantaneous. When the reaction was completed, the mixture was treated with cold water. The organic phase was extracted successively with a 5% HCl aq and with several portions of a 5% NaHCO<sub>3</sub> aq, and then dried over NaSO<sub>4</sub>. After removal of the solvent *in vacuo*, the crude material was quickly distilled through a short vigreux column. The products were monitored by TLC and GLPC. The reported yields are based on the amount of acid chloride used and are corrected on the basis of the actual purity of the product as evidenced by GLPC.

2. *Method B.* Zinc (60 g, 0.92 g-atom) was stirred for 2 hr in a soln of 4 g CuSO<sub>4</sub> in 150 ml water.<sup>5a</sup> The Zn was filtered off, washed with acetone, and dried *in vacuo* at 100°. The activated Zn was placed in a 3-necked round-bottomed flask equipped with a mechanical stirrer, a condenser, and a pressure-equalizing funnel and covered with an ether soln of the diene or the olefin. The acid bromide was added dropwise to the refluxing soln. When the reaction was complete, the excess of Zn was removed by filtration and the filtrate was concentrated *in vacuo*. Addition of hexane under vigorous stirring caused the precipitation of the Zn salts. The liquid was decanted and dried over CaSO<sub>4</sub>. After evaporation of the solvents *in vacuo* the products were purified by fractional distillation.

#### *General procedure for dechlorination with tributyltinhydride*

1. Tributyltinhydride was prepared according to a slight modification of the procedure described.<sup>15</sup> A soln of LAH (4.75 g, 0.136 mole) in 400 ml anhyds ether was placed in a 3-necked round-bottomed flask equipped with a mechanical stirrer, a condenser, and a pressure-equalizing funnel containing 100 g (0.308 mole) of tributyltinchloride (FLUKA). The system was flushed with N<sub>2</sub> and then tributyltinchloride was added dropwise at a rate which maintained a gentle reflux of the ether. The resulting mixture was then stirred for 7 hr. Careful addition of water to the cooled mixture destroyed the excess LAH. The ether soln was decanted, washed with three 100 ml portions water and dried over CaSO<sub>4</sub>. Evaporation of the solvent and distillation under high vacuum gave 68 g (78%) tributyltinhydride (b.p. 68–69°/0.3 mm,  $n_D^{25}$  1.4688) which was kept under argon atmosphere.

2. A soln of freshly distilled tributyltinhydride in cyclohexane was placed into a 3-necked flask equipped with a condenser, a N<sub>2</sub> inlet tube, and a dropping funnel. The flask was flushed with N<sub>2</sub>. Then the soln was refluxed while a conc soln of the chlorinated ketone in cyclohexane containing a catalytic amount of azobisisobutyronitrile (AIBN) was gradually added. The dechlorinated ketone was isolated by direct distillation of the reaction mixture.

#### *7,7-Dichlorobicyclo [3.2.0] hept-2-ene-6-one (3)*

A soln of 96 g (0.95 mole) triethylamine in 500 ml pentane was added over a period of 3.5 hr to a refluxing soln of 129 g (0.875 mole) dichloroacetylchloride and 216 ml (2.62 moles) of freshly distilled cyclopentadiene<sup>3b</sup> in 1 l. pentane. The mixture was refluxed for an additional 2 hr and then allowed to stand overnight at room temp. After work-up, distillation gave 150.6 g of material boiling between 50 and 65°/2 mm which still contained an appreciable amount of dicyclopentadiene. Redistillation gave 119.2 g (77%) 7,7-dichlorobicyclo [3.2.0] hept-2-ene-6-one (b.p. 67–68°/2 mm,  $n_D^{25}$  1.5136) which appeared homogeneous on TLC and on three different GLPC columns (Se-30, QF-1 and 1500-Carbowax); IR: 3050 (w), 2955 (m), 2920 (m), 2855 (m), 1807 (s), 1608 (w), 752 (s), and 728 (s) cm<sup>-1</sup>. Found: C, 47.28; H, 3.41; Cl, 39.85; mol wt 181 (cryosc). Calcd. for C<sub>7</sub>H<sub>8</sub>Cl<sub>2</sub>O: C, 47.49; H, 3.41; Cl, 40.06%; mol wt 177).

#### *Reaction of 3 with sodium methoxide*

A soln of 13.9 g (0.257 mole) NaOMe in 100 ml MeOH was added dropwise to a cooled (–15°) methanolic soln of 3 (30.6 g, 0.173 mole in 50 ml anhyd MeOH). The rate of addition was such as to maintain the mixture below –5°. The soln was neutralised with 5% HCl and a 5% NaHCO<sub>3</sub> aq. After evaporation of the MeOH and extraction with ether, the organic phase was quickly distilled through a short Vigreux column, giving a pale yellow liquid (26.4 g, 73%) (b.p. 89–123°/7 mm). Redistillation gave a pure colourless liquid 4 (b.p. 118.5–119.5°/11 mm),  $n_D^{25}$  1.4904; IR: 3045 (w), 1739 (s), 1620 (w), 1220 (m), 1173 (m), 765 (m), and 702 (m) cm<sup>-1</sup>. Found: C, 45.90; H, 4.72; Cl, 33.64. Calcd. for C<sub>8</sub>H<sub>10</sub>Cl<sub>2</sub>O: C, 45.95; H, 4.82; Cl, 33.92%.

Heating 4 for 2 weeks in refluxing methanolic NaOMe or for 3 hr in refluxing methanolic HCl did not produce any change ( $\nu_{C=C}$  and the signal corresponding to the olefinic protons remained unchanged).

**Reaction of 3 with benzylamine**

A soln of 1 g (5.6 mmoles) of **3** in 2 ml dry ether was treated with 0.61 g (5.7 mmoles) benzylamine. After 1/2 hr the crystals were filtered off and recrystallized from EtOH, yield: 1.54 g pure amide **5** (96.8%) m.p. 131.5–133.5°; IR: (KBr): 3300 (s), 3060 (m), 3040 (m), 3025 (w), 2940 (w), 2915 (m), 2875 (m), 2860 (m), 1633 (s), 1622 (sh), 1545 (m). Found: C, 59.04; H, 5.39; Cl, 24.94; N, 5.11. Calcd for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>NO: C, 59.16; H, 5.32; Cl, 24.95; N, 4.93%.

**Bicyclo [3.2.0] hept-2-ene-6-one (6)**

1. *Dechlorination of 3*. From the reaction of 9.6 g (0.054 mole) of **3** and 31 g (0.108 mole) tributyltinhydride in 30 ml cyclohexane containing 0.1 g (0.6 mmole) AIBN were obtained 4.38 g (75% yield) pure bicyclo [3.2.0] hept-2-ene-6-one (b.p. 62°/20 mm),  $n_D^{25}$  1.4800; IR: 3060 (w), 2950 (m), 2920 (m), 2860 (w), 1786 (s), 1608 (w), 746 (m) and 702 (m) cm<sup>-1</sup>. Found: C, 77.36; H, 7.44. Calcd for C<sub>7</sub>H<sub>8</sub>O: C, 77.75; H, 7.46.

The *semicarbazone* recrystallised from a 3:1 mixture of MeOH-water melted at 218–219° (lit. 219–220°).<sup>37</sup>

2. *Direct synthesis from cyclopentadiene and dichloroketene*. A soln of 13 g (0.129 mole) triethylamine in 50 ml pentane was added dropwise over a period of 2 hr into a refluxing mixture of 18.4 g (0.125 mole) dichloroacetyl-chloride, and 20 g (0.303 mole) cyclopentadiene in 300 ml pentane. After an additional period of 3 hr at reflux temp, the mixture was worked-up as usual and the solvent was removed *in vacuo*. The resulting reddish-brown liquid (25 g) was directly dehalogenated with a soln of 73 g (0.252 mole) tributyltinhydride in 125 ml cyclohexane containing 0.181 g (0.11 mmole) AIBN. Removal of the solvent left a liquid which was shown by GLPC (SE-30 and Apiezon-L) to be a mixture of two components: dicyclopentadiene and bicyclo [3.2.0] hept-2-ene-6-one. Distillation yielded 8.83 g (66%) of the ketone **6**.

**8,8-Dichlorobicyclo [4.2.0] oct-2-ene-7-one (7a)**

1. *Method A*. Triethylamine (32.7 g, 0.324 mole) in 160 ml low-boiling (50–60°) light petroleum was added over a 2 hr period to a refluxing soln of 50 g (0.339 mole) of dichloroacetyl-chloride and 48 g (0.6 mole) cyclohexadiene in light petroleum. After an additional hr at reflux temp the mixture was allowed to stand overnight at room temp. Work-up followed by distillation gave 37.5 g (60%) of a yellowish liquid (b.p. 68–73°/0.4 mm) which appeared homogeneous on TLC and GLPC (SE-30, QF-1 and 1500 carbowax). Redistillation gave pure colourless 8,8-dichlorobicyclo [4.2.0] oct-2-ene-7-one (b.p. 73–74°/1 mm),  $n_D^{25}$  1.5212; IR: 3035 (w), 2935 (m), 2850 (w), 1810 (s), 1649 (w) and 727 (s) cm<sup>-1</sup>. Found: C, 50.19; H, 4.10; Cl, 36.84. Calcd for C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>O: C, 50.29; H, 4.22; Cl, 37.12%.

2. *Method B*. Activated Zn (33 g, 0.5 g-atom) was covered with a soln of 40 g (0.5 mole) cyclohexadiene in 200 ml ether, and 34 g (0.15 mole) trichloroacetyl bromide were added dropwise to the refluxing mixture under vigorous stirring. After 2 hr 1/2 the mixture was worked up. Distillation gave 6 g of **7a** (b.p. 70–85°/1.5 mm); 21% yield.

**Bicyclo [4.2.0] oct-2-ene-7-one (7b)**

From 21.1 g (64.8 mmole) tributyltinhydride, 6.1 g (31.9 mmole) **7a** and 48.4 mg (0.295 mmole) AIBN in 25 ml cyclohexane were obtained 2.05 g (53% yield) **7b** (b.p. 69–78°/15 mm),  $n_D^{25}$  1.4922) homogeneous on GLPC (SE-30, QF-1, Apiezon L); IR: 3025 (m), 2930 (m), 2865 (m), 1782 (s) and 1644 (w).

The *semicarbazone* showed m.p. 200–201° after recrystallization from MeOH-water (lit. 200.5–201°).<sup>37</sup>

**2,2-Dichloro-3-vinylcyclobutanone (8)**

1. *Method A*. To 30 g (0.55 mole) of butadiene (FLUKA, puriss.) condensed in 300 ml cyclohexane were added 31.9 g (0.216 mole) dichloroacetyl chloride. The condenser was continuously flushed with MeOH at –40°. A soln of triethylamine (22 g, 0.218 mole) in 150 ml cyclohexane was added in 5 ml portions over a period of 4 hr. Work-up followed by distillation gave 6.7 g yellow liquid (b.p. 67–84°/0.5 mm), which was shown to be 2,2-dichloro-3-vinylcyclobutanone (purity 88%) on the basis of IR and NMR data.

2. *Method B*. A soln of 14 g (0.06 mole) trichloroacetyl bromide in 50 ml ether was added dropwise to a vigorously stirred mixture of activated Zn (20 g, 0.31 g-atom), butadiene (15 g, 0.28 mole), and 100 ml ether over a period of 2.5 hr. Work-up and distillation gave 3.2 g 2,2-dichloro-3-vinylcyclobutanone (80% purity by GLPC (b.p. 60–74°/4 mm), 23% yield. An analytically pure sample was obtained by preparative GLPC (SE-30); IR: 3015 (w), 1805 (s), 1640 (w), 980 (m) and 930 (m) cm<sup>-1</sup>. (Found: C, 43.61; H, 3.49; Cl, 42.81; O, 9.84. Calcd. for C<sub>6</sub>H<sub>6</sub>Cl<sub>2</sub>O: C, 43.67; H, 3.66; Cl, 42.97; O, 9.70%.)

**Anthracene and dichloroketene**

A soln of 16 g (0.159 mole) triethylamine in 100 ml benzene was added dropwise to a mixture of 23 g dichloroacetylchloride (0.156 mole) and 25 g (0.141 mole) anthracene in 1.35 l. benzene. After work-up, 24.2 g (97%) anthracene were recovered.

**Indene and dichloroketene**

To a refluxing mixture of 67.2 g (0.456 mole) dichloroacetylchloride, 100 g (0.86 mole) indene, and 600 ml low-boiling light petroleum were added gradually 45.5 g (0.45 mole) triethylamine in 300 ml light petroleum. Work-up followed by removal of excess indene (b.p. 30–35°/0.4 mm), left a dark-red residue which crystallized on cooling. Recrystallization from a 50:50 mixture of EtOH-ether gave 41.4 g (41% yield) colourless crystals **10**, m.p. 78–78° 5; IR: (KBr): 1808 (s), 759 (s) and 749 (m)  $\text{cm}^{-1}$ . Found: C, 58.29; H, 3.45; Cl, 31.35. Calcd. For  $\text{C}_{11}\text{H}_8\text{Cl}_2\text{O}$ : C, 58.17; H, 3.55; Cl, 31.23%.

**Reaction of 10 with sodium methoxide**

A methanolic soln of NaOMe (2.3 g, 0.043 mole in 25 ml) was added dropwise to a soln of 9.1 g (0.04 mole) of **10** in a 100 ml ether-MeOH 1:1 mixture. After neutralisation with successive addition of 5% HCl aq and  $\text{NaHCO}_3$  aq, the soln was concentrated *in vacuo* and extracted with ether. Evaporation left 9.7 g (94%) white solid **11** which was recrystallized from methanol (m.p. 43–44°); IR (KBr): 1734 (s), 1228 (s), 762 (m), 733 (m). (Found: C, 55.69; H, 4.63; Cl, 27.30. Calcd. For  $\text{C}_{12}\text{H}_{22}\text{Cl}_2\text{O}_2$ : C, 55.61; H, 4.67; Cl, 27.36%.)

**Dechlorination of 10**

Treatment of 2 g (8.8 mmoles) of **10** with 5.3 g (18 mmoles) tributyltinhydride in 6 ml cyclohexane yielded 0.4 g of **12**. The product was contaminated by a small amount of tributyltinchloride. Preparative GLPC gave a sample which was essentially pure **12**. IR: 1783 (s). (Found: C, 83.07; H, 7.01; O, 10.30. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}$ : C, 83.51; H, 6.37; O, 10.11%.)

**2-Oxa-8, 8-dichlorobicyclo [4.2.0] octan-7-one (13)**

A soln of 43 g (0.42 mole) triethylamine in 175 ml low-boiling light petroleum was added over a period of 3 hr to a mixture of 95.6 g (1.138 mole) dihydropyran and 61.2 g (0.41 mole) dichloroacetylchloride in 375 ml light petroleum. Work-up followed by removal of the solvent and excess of dihydropyran *in vacuo* left an oil which crystallized on cooling. The yield of crystals 27.4 g (35% yield) melting between 61.5° and 68°. The analytical sample had m.p. 68–69.5° after crystallizations from ether and cyclohexane; IR ( $\text{CCl}_4$ ): 2937 (m), 2860 (m), 1818 (s), 1132 (m), 1065 (m), 1040 (s)  $\text{cm}^{-1}$ . (Found: C, 43.26; H, 4.21; Cl, 36.43; O, 16.50. Calcd. for  $\text{C}_7\text{H}_8\text{Cl}_2\text{O}_2$ : C, 43.10; H, 4.13; Cl, 36.36; O, 16.41%.)

**Dehalogenation of 13**

The reaction of 7.5 g (0.04 mole) of **13** with 35.1 g (0.12 mole) tributyltinhydride in 80 ml cyclohexane containing 0.2 g AIBN gave 2.8 g (56%) of **14** (b.p. 84–86°/12 mm),  $n_D^{20}$  1.4628; IR: 2920 (s), 2842 (m), 1780 (s), 1068 (m), 1050 (m) and 1035 (m)  $\text{cm}^{-1}$ .

**7,7-Dichlorobicyclo [3.2.0] heptan-6-one (15)**

1. **Method A.** A mixture of triethylamine (36 g, 0.356 mole) in 100 ml cyclopentene was added to a refluxing soln of 50.1 g (0.34 mole) dichloroacetylchloride in 300 ml cyclopentene. Work-up and distillation gave 41.1 g (68%) of a yellowish liquid, b.p. 53–62°, which was shown to be 7,7-dichlorobicyclo [3.2.0] heptan-6-one. Redistillation gave pure material (b.p. 73°/1.5 mm,  $n_D^{25}$  1.4999). (Found: C, 46.76; H, 4.60; Cl, 39.45. Calcd. for  $\text{C}_7\text{H}_8\text{Cl}_2\text{O}$ : C, 46.95; H, 4.50; Cl, 39.61%.)

2. **Method B.** A soln of 15.8 g (0.07 mole) trichloroacetyl bromide in 50 ml dry ether was added dropwise into a vigorously stirred mixture of activated Zn (13 g, 0.21 g-atom), cyclopentene (14.2 g, 0.21 mole), and dry ether (100 ml). Work-up and distillation gave 2.8 g 7,7-dichlorobicyclo [3.2.0] heptan-6-one.

**8,8-Dichlorobicyclo [4.2.0] octan-7-one (16a)**

1. **Method A.** A soln of 20.9 g (0.207 mole) triethylamine in 140 ml cyclohexane was added over a period of 1 hr to a mixture of 30.6 g (0.207 mole) dichloroacetylchloride in 275 ml cyclohexane at 65°. After an additional hr at reflux temp, the mixture was worked up. Distillation gave a fraction (23 g, 57%), (b.p. 65–120°/0.5 mm), which was shown to contain 93% of 8,8-dichloro-bicyclo [4.2.0] octan-7-one on the basis of



GLPC (SE-30, QF-1 and Apiezon L), IR and NMR data. The adduct was thermally sensitive and could not be obtained analytically pure. It was immediately dehalogenated with tributyltinhydride to give the known **16b** (b.p. 40–55°/0.3 mm).<sup>17</sup> The *semicarbazone* had a m.p. 171–173° after recrystallization from ethanol-water (lit. 164–166°); IR of **16**: 2930 (s), 2855 (m), 1800 (s), 1488 (m) cm<sup>-1</sup>.

2. *Method B*. A soln of 34 g (0.15 mole) trichloroacetyl bromide in 50 ml dry ether was added dropwise into a stirred mixture of activated Zn (33 g, 0.5 g-atom), cyclohexene (41 g, 0.5 mole) and 200 ml dry ether. Work-up and distillation gave 4.4 g (23%) of **16a**.

#### 4,4-Dichloro-exo-tricyclo [4.2.1.0<sup>2,3</sup>] nonan-3-one (**17**)

Triethylamine (21 g, 0.2 mole) was added over a period of 2 hrs to a refluxing mixture of 30 g (0.2 mole) dichloroacetyl chloride and 40 g (0.42 mole) norbornene in 200 ml petroleum ether (b.p. 60–70°). After an additional 30 minutes the mixture was worked up. A quick distillation gave a 4 g yellow fraction distilling between 62 and 80°/2 mm which was shown by GLPC (SE-30 and Apiezon L) to contain **17** in 83% purity. Careful redistillation led only to extensive decomposition.

IR: 2970 (m), 2890 (m), 1804 (s), 1457 (m).

The *dechlorination* of **17** with tributyltinhydride gave the known *exo-tricyclo* [4.2.1.0<sup>2,3</sup>] nonan-3-one (**18**), IR (CCl<sub>4</sub>): 2965 (m), 2875 (w), 178 (s), identical with the product previously obtained.<sup>21</sup>

#### 4,4-Dichloro-exo-tricyclo [4.2.1.0<sup>2,3</sup>] non-7-ene -3-one (**20**)

A refluxing mixture of 101.4 g (0.688 mole) dichloroacetyl chloride and 168 g (1.83 mole) norbornadiene in 600 ml light petroleum (50–60°) was treated over a period of 6 hr with 75 g (0.74 mole) triethylamine in 300 ml light petroleum. After standing overnight, the mixture was worked-up and distilled yielding 34.5 g (25%) of **20** (83% pure GLPC SE-30 and QF-1). Redistillation gave a colourless liquid (b.p. 76°/1 mm,  $n_D^{25}$  1.5296); IR: 3066 (w), 2985 (m), 2980 (w), 1804 (s), 1564 (w).

The *adduct 20* was directly *dechlorinated* by the standard procedure giving the parent ketone **22** (53%) (b.p. 66–68°/6 mm,  $n_D^{25}$  1.5050); IR (CCl<sub>4</sub>): 3065 (w), 2975 (m), 2890 (w), 1778 (s), 1569 (w). (Found: C, 80.39; H, 8.8-02. Calcd. for C<sub>9</sub>H<sub>10</sub>O: C, 80.56; H, 7.51%).

After 3 days at room temp in the presence of an equiv amount of phenylazide, compound **22** gave a solid adduct **23** which, after recrystallization from ethanol, had m.p. 190–192°. Found: C, 71.27; H, 5.61; N, 16.66; O, 6.47. Calcd. for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O: C, 71.12; H, 5.97; N, 16.59; O, 6.326%.

*Compound 22* was shown to absorb the *theoretical amount of hydrogen* when exposed to *Adam's catalyst* in ethanol. The spectral data of the hydrogenation product were identical with those of **18**.

#### endo-Dicyclopentadiene and dichloroketene

Cyclopentadiene (prepared by depolymerisation of commercial dicyclopentadiene) was allowed to dimerize at 0° for a few days. Distillation (b.p. 53°/8.5 mm) gave pure *endo*-dicyclopentadiene,<sup>18</sup> m.p. 32.5°. To a refluxing mixture of 44.2 g (0.3 mole) dichloroacetyl chloride and 168 g (1.27 mole) *endo*-dicyclopentadiene in 1 l. light petroleum (50–60°) was added over 2 hr a soln of 30.3 g (0.3 mole) triethylamine in 300 ml light petroleum. Work-up and distillation gave 42 g (58%) of a homogeneous adduct **24** (b.p. 95–108°/0.1–0.2 mm), which crystallized on cooling. Three recrystallizations from EtOH gave white crystals, m.p. 54–55°; IR (CCl<sub>4</sub>): 3060 (w), 2970 (m), 2940 (m), 2875 (w), 1805 (s), 1449 (m), 1347 (m). (Found: C, 59.22; H, 4.84; Cl, 29.30. Calcd. for C<sub>12</sub>H<sub>12</sub>Cl<sub>2</sub>O: C, 59.27; H, 4.97; Cl, 29.16%).

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