Addition of Chloroketens to Spiro[2.4]hepta-4,6-diene

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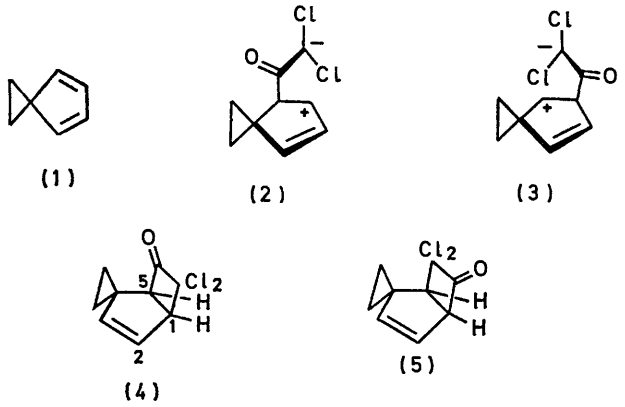
Addition of chloroketens to spiro[2.4]hepta-4,6-diene is regiospecific, giving 7-chlorospiro(bicyclo[3.2.0]hept-2-ene-4,1'-cyclopropan)-6-ones (6)—(10) rather than the 6-chloro-7-ketones. For alkyl-substituted chloroketens there was an increase in the proportion of 7-*endo*-alkyl adduct as the size of the alkyl group increased supporting a crosswise approach of the keten and spirodiene. Phenyl(chloro)keten yielded a single 6-keto-adduct with dimethylfulvene.

THE addition of ketens to cyclopentadiene gives bicyclo-[3.2.0]hept-2-en-6-ones regiospecifically. The result is readily accounted for if it is assumed that the cycloaddition is not completely concerted and some charge develops in the transition state.[1] The partially charged species leading to bicyclo[3.2.0]hept-2-en-6-ones is stabilised by allylic resonance; that leading to the corresponding 7-ketones is not.

It has been argued that a dipolar species intervenes in keten–olefin additions, but any such species must be extremely short lived, with ring-closure being faster than rotation about bonds in order to explain stereospecific additions to *cis*- and *trans*-olefins.[2] Further, no anomalous additions have been observed where non-classical cationic species could reasonably be expected if a dipolar intermediate intervened.[3]

When cycloadditions of ketens to spiro[2.4]hepta-4,6-diene (1) are considered, the difference in stability between the two transition states leading respectively to the 6- and 7-ketone is lessened. For example, in the addition of dichloroketen to the spirodiene the 6-ketone (4) is derived from a transition state having some of the character of the formal dipole (2) while the 7-ketone (5) involves a transition state related to (3). In (2) the positive charge is fully conjugated with the double bond and the cyclopropane fixed in the correct bisected form. The positive charge in (3) is less fully conjugated, but nevertheless should possess considerable stability being of the cyclopropylcarbinyl type. We suggest that the greater the charge separation in the transition state for such cycloadditions the more selective they will be. Conversely, if charge separation is only slight both 6- and 7-keto-compounds should be formed † [examination of models in order to estimate steric factors suggests that the cyclopropyl methylene group of the spiro-diene (1) should give little more interference with the crosswise approach of the keten than the methylene group in cyclopentadiene].



Dichloroketen reacted readily with the spirodiene to yield 85% of a single dichlorocyclobutanone (ν_{CO} 1807 cm^{-1}), either (4) or (5), which by g.l.c. and n.m.r. analysis was at least 98% pure. The n.m.r. spectrum showed separate signals for each olefinic and bridgehead proton (H-1, H-2, H-3, and H-5) with a complex (ABCD) multiplet at higher field for the cyclopropyl protons, and was readily interpreted. To assign the correct structure to the adduct avoiding arguments as to the expected chemical shifts of H-1 and H-5 in the two ketones (4) and (5), it was treated with sodium hydroxide and

† If $\Delta\Delta G^{\ddagger}$ for the two transition states is less than 10 kJ mol^{-1}, the 7-ketone (5) should be detectable.

[1] (*a*) R. Huisgen and P. Otto, *Chem. Ber.*, 1969, 3475; (*b*) L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Letters*, 1966, 135.

[2] A. Gompper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312; H. U. Wagner and R. Gompper, *Tetrahedron Letters*, 1970, 2819; R. Montaigne and L. Ghosez, *Angew. Chem. Internat. Edn.*, 1968, **7**, 221.

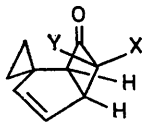
[3] P. R. Brook and J. G. Griffiths, *Chem. Comm.*, 1970, 1344.

yielded the ring-opened spiro-acid [4] (11) (note change in numbering). In its n.m.r. spectrum the doublet for $CHCl_2$ (δ 6·27, J 9·5 Hz) was clearly coupled to the most complex signal in the lower field part of the spectrum, that of H-5 which was also coupled to H-4, H-6, and H-7. Thus the adduct was the 6-ketone (4) and the course of the reaction was the same as for cyclopentadiene [the 7-ketone would give an acid related to (11) but with CO_2H and $CHCl_2$ groups interchanged].

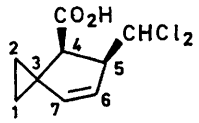
Methyl(chloro)keten with the spirodiene (1) gave a mixture of 7-*endo*-methyl- and 7-*exo*-methyl epimers [respectively (6) and (7); ratio 78 : 22] in high yield. The 6-keto-structure for these compounds was assigned by comparison of the n.m.r. spectra with those for the dichloroketen adduct (4) and the corresponding three adducts for cyclopentadiene.[5] For adducts (4), (6), and (7) the effect of the cyclopropane ring on the chemical shifts of H-1 and H-5 when compared with those for cyclopentadiene-adducts was quite uniform: H-1 was deshielded by 0·1—0·2 p.p.m., while H-5 was shielded and brought upfield by 0·5—0·6 p.p.m. A related upfield shift was observed for H-3. These shifts are as expected for the anisotropy of the cyclopropane ring system.[6]

Confirmation of the stereochemistry at C-7 in the methyl(chloro)keten adducts was obtained when the *endo*-methyl-epimer (6) was treated with base to give the ring contracted *exo*-spirotricyclo-octene acid (13) stereospecifically; the *exo*-methyl epimer (7) similarly yielded the *endo*-acid (12). This stereospecific ring contraction has been noted in simple monohalogenocyclobutanones by Conia,[7] and also in monochloroketen–cyclopentadiene adducts.[5b] The *endo*-acid (12) when treated with iodine–sodium hydrogen carbonate readily gave a mixture of the γ- and δ-iodo-lactones [respectively (16) and (17)] in a ratio of *ca.* 1 : 2, thus confirming its stereochemistry and hence that of the minor product of this cyclo-addition (7).

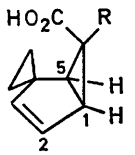
In a similar way, isopropyl(chloro)keten and the spirodiene (1) yielded a mixture of epimeric adducts (8) and (9) with the major product having the isopropyl group *endo* [ratio of (8) and (9), 91 : 9]. Ring-contraction of the minor product (9) proceeded readily as before to yield the *endo*-tricyclic acid (14) stereospecifically. This acid formed γ- and δ-iodo-lactones (18) and (19), but in contrast to the methyl series the γ-lactone (18) was the major product.* Base treatment of the epimeric isopropyl adduct (8) failed to give the *exo*-acid (15). In this case the required conformation of the cyclobutane ring (20) with equatorial chlorine requires an axial isopropyl group which produces a severe 1,3-diaxial interaction across the cyclobutane ring. We have reported similar failure of ring contraction in the corresponding cyclopentadiene adduct lacking the spirocyclopropane ring.[8]



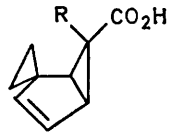
(6) X = Cl, Y = Me
(7) X = Me, Y = Cl
(8) X = Cl, Y = Pr^i
(9) X = Pr^i, Y = Cl
(10) X = Cl, Y = Ph



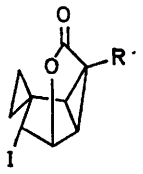
(11)



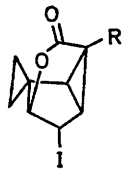
(12) R = Me
(14) R = Pr^i



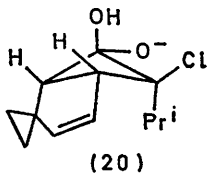
(13) R = Me
(15) R = Pr^i



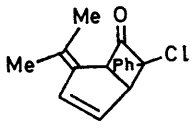
(16) R = Me
(18) R = Pr^i



(17) R = Me
(19) R = Pr^i



(20)



(21)

Phenylchloroketen gave only one adduct which from spectral data was assigned the *endo*-phenyl structure (10).

The foregoing cycloadditions to spirodiene (1) provide regiospecific and stereoselective results almost identical with those for cyclopentadiene itself. We conclude that the keten approaches the diene in a crosswise manner as previously described,[5] and that considerable charge is developed in the transition state to account for the regiospecificity.

The arguments put forward above as to the amount of

* This change in the proportion of γ- and δ-iodo-lactones in going from the methyl to the isopropyl series may reflect the varying ability of the substituted cyclopropane to stabilise the partial positive charge of the intermediate iodonium ion at C-2 when compared with the spiro-cyclopropane stabilising charge at C-3 (electron donating effect of Me *v.* Pr^i).

[4] For similar ring-opening reactions see (*a*) J. M. Conia and J. L. Ripolin, *Bull. Soc. chim. France*, 1963, 765; (*b*) P. R. Brook and A. J. Duke, *J. Chem. Soc.* (*C*), 1971, 1764; and ref. 1*b*.

[5] (*a*) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, 1970, **53**, 417; (*b*) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Comm.*, 1970, 589; (*c*) W. T. Brady and R. Roe, *J. Amer. Chem. Soc.*, 1970, **92**, 4618.

[6] For a discussion of this anisotropy in rigid ring systems see K. Tori and K. Kitahonoki, *J. Amer. Chem. Soc.*, 1965, **87**, 386, and H. Prinzbach, W. Eberbach, M. Klaus, and A. Veh, *Chem. Ber.*, 1968, **101**, 4066.

[7] J. M. Conia and J. R. Salaun, *Accounts Chem. Res.*, 1972, **5**, 33.

[8] P. R. Brook and J. M. Harrison, *J.C.S. Chem. Comm.*, 1972, 997.

charge developed in the transition state of keten–olefin additions also apply to cycloadditions to fulvenes where the exocyclic double bond replaces the cyclopropane ring. The partial positive charge in the transition state leading to 6-keto-adducts is fully conjugated with the diene system; that for 7-keto-adducts is stabilised, but in a cross conjugated system. Phenyl(chloro)keten with 6,6-dimethylfulvene yielded a single adduct. Using the result of similar reactions with fulvenes [9] we assign the adduct structure (21).

EXPERIMENTAL

For details of experimental techniques and experimentation, see ref. 4*b*.

Addition of Chloroketens to Spiro[2.4]*hepta*-4,6-*diene* (1).—As a general procedure, the appropriate chloroacyl chloride was added dropwise over *ca.* 3—5 min to a rapidly stirred mixture of 1 equiv. of triethylamine in a 3- to 5-fold excess of the spirodiene and an equal volume of pentane. After a further 5 min the mixture was poured into water, the organic phase was washed with 2N-sodium carbonate, 2N-hydrochloric acid, and water, and after removal of solvent and excess of spirodiene the crude product was analysed by n.m.r. Where stereoisomers were present chromatography with benzene–petroleum (b.p. 60—80°) (1 : 1) as eluant gave complete separation.

(a) 7,7-*Dichlorospiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1′-*cyclopropan*)-6-*one* (4).—Dichloroacetyl chloride (2·3 g, 0·015 mol) in this way gave the tricyclic *dichloro-ketone* (4) (2·59 g, 85%) as a liquid, b.p. 71—72° at 0·65 mmHg, which slowly crystallised on standing at −50°, m.p. 28° (Found: C, 52·7; H, 3·95; Cl, 34·8. $C_9H_8Cl_2O$ requires C, 53·2; H, 3·9; Cl, 34·8%), $\nu_{max.}$ 1807 (C=O) and 1600 cm^{-1} (C=C), δ 5·66 (1H, dd, *J* 2·2 and 5·0 Hz, H-2), 5·52 (1H, dd, *J* 1·4 and 5·0 Hz, H-3), 4·17 (1H, d, with further small couplings, *J* 7·6 Hz, H-1), 3·72 (1H, d, *J* 7·6 Hz, H-5), and 1·4—0·55 (4H, m, cyclopropyl CH_2). The compound was homogeneous by g.l.c.

(b) exo-7-*Chloro*-7-*phenylspiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1′-*cyclopropan*)-6-*one* (10).—Phenyl(chloro)acetyl chloride (0·95 g, 0·005 mol) gave the *spiro-phenyl ketone* (10) (95%), b.p. 110° at 0·07 mmHg, m.p. 67·5—68° (from hexane) (Found: C, 73·8; H, 5·25; Cl, 14·95. $C_{15}H_{13}ClO$ requires C, 73·6; H, 5·3; Cl, 14·5%), $\nu_{max.}$ 1788 cm^{-1} (C=O), δ 7·6—7·15 (5H, m, aromatic), 5·28 (2H, s, olefinic), 4·21 (1H, dd, *J* 1·0 and 7·5 Hz, H-1), 3·79 (1H, d, *J* 7·5 Hz, H-5), and 1·45—0·45 (4H, m, cyclopropyl). The compound gave one spot by t.l.c.

(c) *Epimeric* 7-*Chloro*-7-*methylspiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1′-*cyclopropan*)-6-*ones* (6) *and* (7).—2-Chloropropionyl chloride (3·18 g, 0·025 mol) gave a mixture of 7-*endo*-methyl- and 7-*exo*-methyl-spirochloroketones, respectively (6) and (7), in a ratio of 78 : 22 (88%).

On chromatography the endo-*methyl ketone* (6), b.p. 75° 0·1 mmHg, was eluted first and was shown to be homogeneous by g.l.c. (3·10 g, 68%) (Found: C, 65·75; H, 6·3; Cl, 19·65. $C_{10}H_{11}ClO$ requires C, 65·75; H, 6·0; Cl, 19·4%), $\nu_{max.}$ 1792 cm^{-1} (C=O), δ 5·68 (1H, dd, *J* 2·1 and 5·6 Hz, H-2), 5·45 (1H, dd, *J* 1·2 and 5·5 Hz, H-3), 3·82 (1H, d, *J* 8·0 Hz with further splitting, H-1), 3·65 (1H, d, *J* 8·0 Hz, H-5), 1·53 (3H, s, Me), and 1·41—0·43 (4H, m, cyclopropyl).

The *spiro*-exo-*methyl ketone* (7) was eluted next and after bulb-to-bulb distillation crystallised, m.p. 41—44° (0·91 g, 20%) (Found: C, 65·4; H, 5·95; Cl, 19·2%), $\nu_{max.}$ 1796 cm^{-1} (C=O), δ 5·65 (1H, dd, *J* 2·4 and 5·6 Hz, H-2), 5·38 (1H, dd, *J* 1·5 and 5·6 Hz, H-3), 3·70 (1H, d, *J* 7·5 Hz with further coupling, H-1), 3·33 (1H, d, *J* 7·5 Hz, H-5), 1·73 (3H, s, Me), and 1·39—0·49 (4H, m, cyclopropyl).

(d) *Epimeric* 7-*chloro*-7-*isopropylspiro*(*bicyclo*[3.2.0]*hept*-2-*ene*-4,1′-*cyclopropan*)-6-*ones* (8) *and* (9).—2-Chloro-3-methylbutyryl chloride (8·27 g, 0·054 mol) was added in the same way, but unlike the earlier additions the reactants were then heated under reflux for 3 h. Usual work-up gave a mixture of crude adducts (8) and (9) containing 90% endo-*isopropyl epimer* (8) (g.l.c.) which was eluted first on chromatography (7·50 g, 74%), b.p. 88° at 0·8 mmHg, m.p. 39—40·5° (Found: C, 68·4; H, 7·0; Cl, 16·8. $C_{12}H_{15}ClO$ requires C, 68·4; H, 7·1; Cl, 16·9%), $\nu_{max.}$ 1790 cm^{-1} (C=O), δ 5·71 (1H, dd, *J* 1·8 and 5·0 Hz, H-2), 5·49 (1H, dd, *J* 1·2 and 5·0 Hz, H-3), 3·81 (1H, d, *J* 8·0 with further coupling, H-1), 3·60 (1H, d, *J* 8·0 Hz, H-5), 2·28 (1H, septet, C*H*Me$_2$), and 1·4—0·45 (10H, m, cyclopropyl CH_2 and apparent t, CH*Me*$_2$).

The exo-*isopropyl epimer* (9) was eluted next (0·85 g, 8%); after bulb-to-bulb distillation, b.p. 90° at 0·5 mmHg, it had m.p. 33—33·5° (Found: C, 68·0; H, 6·9; Cl, 16·65%), $\nu_{max.}$ 1788 cm^{-1} (C=O), δ 5·58 (1H, dd, *J* 2·3 and 5·3 Hz, H-2), 5·35 (1H, dd, *J* 1·3 and 5·3 Hz, H-3), 3·72 (1H, d, *J* 7·9 Hz with further splitting, H-1), 3·23 (1H, d, *J* 7·9 Hz, H-5), 2·15 (1H, septet, C*H*Me$_2$), 1·08 and 1·02 (6H, 2 overlapping d, CH*Me*$_2$), and 1·4—0·48 (4H, m, cyclopropyl CH_2). Isolated yield, 82%, ratio 91 : 9.

Reactions of the Spiro-adducts with 2N-*Sodium Hydroxide.*—(a) cis-5-*Dichloromethylspiro*[2.4]*hept*-6-*ene*-4-*carboxylic acid* (11). The spiro-dichloroketone (4) (203 mg, 0·001 mol) was shaken at room temperature with sodium hydroxide (2N; 10 ml) for 0·5 h. The alkaline solution was washed with chloroform, acidified to pH 1, and was then extracted with chloroform to give the *spiro-acid* (11) (200 mg, 90%), m.p. 82·5—84° after sublimation *in vacuo* (90° at 0·5 mmHg) (Found: C, 48·55; H, 4·7; Cl, 32·4. $C_9H_{10}Cl_2O_2$ requires C, 48·9; H, 4·5; Cl, 32·1%), $\nu_{max.}$ 2750, 2665 (OH), 1706, and 1695sh cm^{-1} (C=O), δ 10·99 (1H, s, OH), 6·27 (1H, d, *J* 9·5 Hz, $CHCl_2$), 5·78 (1H, dd, *J* 1·8 and 6·0 Hz, H-6), 5·48 (1H, dd, *J* 2·3 and 6·0 Hz, H-7), 3·98 (1H, apparent t with multiple couplings *J* 9·5, 8·2, 2·3, and 1·8 Hz, H-5), 3·05 (1H, d, *J* 8·2 Hz, H-4), and 1·11—0·68 (4H, m, cyclopropyl CH_2).

(b) 6-*Methylspiro*(*bicyclo*[3.1.0]*hex*-2-*ene*-4,1′-*cyclopropane*)-6-exo-*carboxylic acid* (13). The spiro-*endo*-methyl chloro-ketone (6) (200 mg, 0·00104 mol) after shaking with sodium hydroxide (2N; 10 ml) for 30 min gave the *spiro*-endo-*methyl*-exo-*acid* (13) from aqueous methanol, m.p. 87—88° (166 mg, 98%) (Found: C, 73·15; H, 7·25. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%), $\nu_{max.}$ 2620br, 1685, and 1675 cm^{-1} (C=O), δ 12·23 (1H, s, OH), 5·67 (1H, dd, *J* 2·2 and 5·2 Hz, H-2), 5·32 (1H, broadened d, *J* 5·2 Hz, H-3), 2·78 (1H, dd, *J* 2·2 and 7·0 Hz, H-1), 2·01 (1H, broadened d, *J* 7·0 Hz, H-5), 1·44 (3H, s, Me), and 1·05—0·50 (4H, m, cyclopropyl CH_2).

(c) 6-*Methylspiro*(*bicyclo*[3.1.0]*hex*-2-*ene*-4,1′-*cyclopropane*)-6-endo-*carboxylic acid* (12). The *exo*-methyl spirochloro-ketone (7) (110 mg, 0·0006 mol) in the same way as above gave the *spiro*-exo-*methyl*-endo-*acid* (12) from aqueous methanol, m.p. 80—80·5° (96 mg, 96%) (Found: C, 73·3; H, 7·35%), $\nu_{max.}$ 2730, 2620br (OH), and 1695 cm^{-1}

[9] R. E. Harman, W. D. Borta, S. K. Gupta, and G. Slomp, *Chem. Comm.*, 1970, 935.

(C=O), δ 11·05 (1H, s, OH), 5·71 (1H, dd, *J* 2·2 and 5·1 Hz, H-2), 5·13 (1H, dd, *J* 1·1 and 5·1 Hz, H-3), 2·22 (1H, dd, *J* 2·2 and 6·2 Hz, H-1), 1·43 (1H, broad d, *J* 6 Hz, H-5), 1·28 (3H, s, Me), and 1·30—0·45 (4H, m, cyclopropyl CH_2).

G.l.c. analysis of the methyl ester of this acid showed it to be homogeneous.

Treatment of the *endo*-acid (159 mg) with sodium hydrogen carbonate–potassium triodide yielded a mixture of γ- and δ-iodolactones respectively (16) and (17) (ν_{CO} 1769 and 1735 cm^{-1} respectively) in an approximate ratio of 1 : 2 (246 mg, 96%). Crystallisation of the mixture from methylcyclohexane gave a sample, m.p. 131—135° (Found: C, 41·6; H, 3·95) * whilst after preparative t.l.c. 2-exo-*iodo*-6-exo-*methylspiro*(*bicyclo*[3.1.0]*hexane*-4,1′-*cyclopropan*)-6,3-endo-*olactone* (17), m.p. 138—139°, was obtained (Found: C, 41·3; H, 3·75; I, 43·45. $C_{10}H_{11}IO_2$ requires C, 41·4; H, 3·8; I, 43·75%), ν_{CO} ($CHCl_3$) 1735 cm^{-1}.

(d) 6-*Isopropylspiro*(*bicyclo*[3.1.0]*hex*-2-*ene*-4,1′-*cyclopropane*)-6-endo-*carboxylic acid* (14). The *exo*-isopropylspirochloroketone (9) (140 mg, 0·00066 mol) shaken with sodium hydroxide (2N; 10 ml) for 36 h gave the *spiro*-exo-*isopropyl*-endo-*carboxylic acid* (14), homogeneous by g.l.c. analysis of its methyl ester; after sublimation *in vacuo* its m.p. was 86° (Found: C, 74·8; H, 8·4. $C_{13}H_{16}O_2$ requires C, 75·0; H, 8·4%), $\nu_{max.}$ 2600 (OH) and 1690 cm^{-1} (C=O), δ 10·38 (1H, s, OH), 5·76 (1H, dd, *J* 2·2 and 5·6 Hz, H-2), 5·04 (1H, dd, *J* 1·2 and 5·6 Hz, H-3), 2·12 (1H, dd, *J* 2·2 and 6·3 Hz, H-1), and 1·5—0·5 (12H, m, H-5, cyclopropyl CH_2 and isopropyl group).

Treatment of the acid with sodium hydrogen carbonate–potassium triodide yielded two isomeric iodolactones separable by chromatography. The major product, 3-exo-*iodo*-6-exo-*isopropylspiro*(*bicyclo*[3.1.0]*hexane*-4,1′-*cyclopropan*)-6,2-endo-*olactone* (18) was eluted first, m.p. 64° (from methanol) (Found: C, 45·25; H, 4·65; I, 39·95. $C_{12}H_{15}IO_2$ requires C, 45·3; H, 4·7; I, 39·7%), ν_{CO} ($CHCl_3$) 1770 cm^{-1}. The minor product 2-exo-*iodo*-6-exo-*isopropylspiro*(*bicyclo*[3.1.0]*hexane*-4,1′-*cyclopropan*)-6,3-endo-*olactone* (19) was next eluted, m.p. 65·5—66° (from aqueous methanol) (Found: C, 45·25; H, 4·75; I, 39·7%), ν_{CO} ($CHCl_3$) 1735 cm^{-1}.

(e) *Reaction of the* endo-*isopropyl spiro-chloro-ketone* (8) *with sodium hydroxide*. Treatment of this chloro-ketone did not give any acidic product.

7-exo-*Chloro*-4-*isopropylidene*-7-*phenylbicyclo*[3.2.0]*hept*-2-*en*-6-*one* (21).—Phenyl(chloro)acetyl chloride (2·19 g, 0·0015 mol) was added dropwise over 2 min to a rapidly stirred mixture of 6,6-dimethylfulvene (4·90 g, 0·0462 mol) and triethylamine (1·5 g, 0·0149 mol) in pentane (10 ml). After 10 min, work-up in the usual way gave the 4-*isopropylidene* endo-*phenylbicycloheptenone* (21) as a viscous liquid after bulb-to-bulb distillation, b.p. 130° at 0·1 mmHg (2·40 g, 80%). The adduct rapidly darkened at room temperature and satisfactory microanalytical data were only obtained on freshly distilled samples (Found: C, 74·0; H, 5·75; Cl, 13·95. $C_{16}H_{15}ClO$ requires C, 74·3; H, 5·8; Cl, 13·7%), $\nu_{max.}$ 1789 (C=O) and 1662 cm^{-1} (olefin), δ 7·5—7·1 (5H, m, aromatic H), 6·31 (1H, dd, *J* 1·6 and 5·5 Hz, H-2), 5·48 (1H, broadened dd, H-3), 4·80 (1H, broad d, *J* 7 Hz, H-5), 4·05 (1H, very broad d, *J ca.* 7 Hz, H-1), 1·98br (3H, s, Me), and 1·75br (3H, s, Me). T.l.c. and the n.m.r. spectrum indicated the formation of only one isomer in the cycloaddition.

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* As the analysis of this mixture of γ- and δ-iodolactones was in agreement with that for the pure δ-iodolactone we include it as supporting evidence for the γ-iodolactone structure.