The Type A Zwitterion in Cyclohexadienone Photochemistry: Chemical Trapping and Stereochemistry

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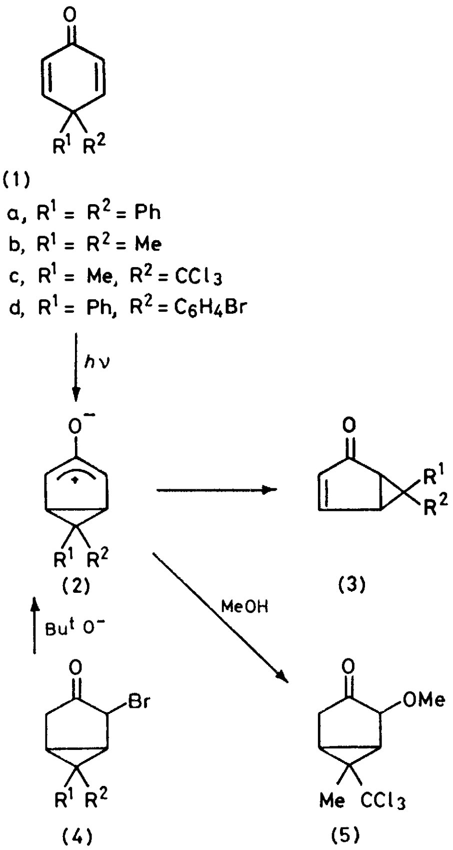
Irradiation of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone in the presence of cyclopentadiene gives two 1 : 1 adducts whose structures demonstrate the intermediacy of the type A zwitterion and whose stereochemistry shows that the walk rearrangement to the lumiketone proceeds with inversion of configuration.

MOST of the photochemistry of the cross-conjugated cyclohexadienones (1) [1,2] has been interpreted in terms of a mechanistic scheme, first proposed by Zimmerman and Schuster [3], involving 3,5-bonding in the ^3n–π^* excited state to form, after electron demotion, a zwitterionic intermediate (2) which can then undergo a walk rearrangement to give the lumiketone (3) or react in other ways (Scheme).



SCHEME

Finding that (1b) undergoes the same rearrangement, both in a polar solvent and in the gas phase, Swenton *et al.*[4] questioned the ionic character of (2) arguing that such a species would be energetically inaccessible in the gas phase. Woodward and Hoffmann[5] have analysed the reaction as $_{\sigma}2_a + _{\pi}2_a$ and pointed out that the concerted process (1) ⟶ (3) directly is photochemically allowed. More recently, Mock and Rumon[6] have tried to test for this by studying a constrained cyclohexadienone, but their negative result is inconclusive.

Zimmerman[7] has reinforced his original suggestion by finding that (4a) undergoes an anomalous Favorskii rearrangement to give (3a). Schuster,[8] too, has provided suggestive evidence in his finding that (1c) gives a solvent adduct (5) on irradiation in acidic methanol. This is the only product yet described in which the C(3)—C(5) cyclopropane ring present in the zwitterion (2) is intact in an isolable product. Even this finding, however, while strongly suggesting the intermediacy of (2c) can be rationalised in terms of other ionic mechanisms.

Schuster's kinetic studies[9] of the irradiation of (1c) in the presence of nucleophiles show that the lumiketones and the trapping products have a common precursor which is not a precursor to *p*-cresol. Assuming that all the products are formed from the ^3n–π^*, and the $^3\pi$–π^* is not involved,[10,11] it is most reasonable to identify this precursor as the zwitterion.

In order to rationalise the stereochemistry at C(6) of the lumiketones, Rodgers and Hart[12] invoked a bridging step, (1*) ⟶ (2), in which steric interaction between the 4-substituents and those at C(3) and C(5) is the controlling factor, followed by a walk step which proceeds with inversion of configuration at the migrating carbon atom (*i.e. exo* remains *exo*) as is allowed in the ground state. While Zimmerman[7] has shown that (4d) gives (3d) with exclusive inversion, it is not established that this relates to the photochemical process. Furthermore the Rodgers and Hart generalisation that the larger group takes up the *endo*-position in the lumiketones does not always hold.[10a,13] Schuster's rationale[10a] for the case of (1c) also depends on the walk step proceeding with inversion of configuration.

In no stereochemically unconstrained case has the stereochemistry of the bridging and walk steps been separated. Schuster[10] has chosen to study an optically active ketone and relate the configurations of dienone and lumiketone. The approach described here[14] involves trapping the zwitterion,[15] which is an oxyallyl cation, using a diene, a method used successfully in the superficially similar photochemistry of 4-pyrones.[16]

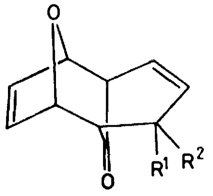
RESULTS

Furan Trapping.—The initial attempts proved abortive. Irradiation of (1b) in furan gave a crystalline 1 : 1 adduct of structure (6a). This compound was previously reported by Chapman *et al.*[17] from irradiation of (3b) in the presence of furan. Presumably the type A zwitterion (2b) is too short-lived to be trapped, but goes on to (3b) which absorbs a second photon and it is the type B zwitterion or the corresponding cyclopropanone which is trapped.

Anticipating that the walk rearrangement of (2c) would be slower than that of (2b), as pointed out by Schuster,[2] (1c) was irradiated in furan to give a single photoproduct isolated by p.l.c. as an unstable oil which darkened on standing. On the basis of its spectroscopic data, structure (7) was assigned.

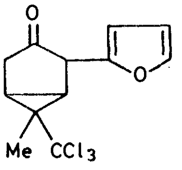
Careful examination of the n.m.r. spectrum when (1c) was irradiated in furan in an n.m.r. tube showed that, at low conversions, a different product was formed but on prolonged irradiation this was destroyed and adduct (7) was formed. It was considered that this might be cycloadduct (8) which was converted into (7) by hydrogen chloride formed as a product of some side reaction.

Accordingly, (1c) was irradiated in furan containing an excess of triethylamine. After removal of the excess of furan, amine, and amine hydrochloride, the n.m.r. spectrum of the crude product showed signals appropriate to adduct (8). The values of the coupling constants and analogy with the cyclopentadiene adducts (see below) suggest that the stereochemistry is as shown. Addition of a trace of trifluoroacetic acid or chromatography on silica gel or neutral or basic alumina resulted in conversion of the product into (7), so purification and characterisation proved impossible.



(6)

a, $R^1 = R^2 = Me$
b R = Me, $R^2 = CCl_3$



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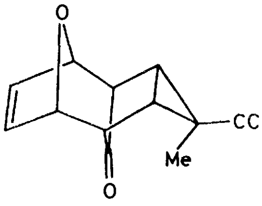
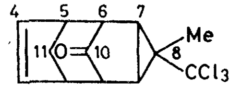


(8)

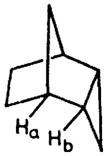
Cyclopentadiene Trapping.—Irradiation of (1c) in benzene containing 10% freshly cracked cyclopentadiene gave, in addition to the bicycloheptenone, previously reported by Schuster[18] and shown to derive from secondary photolysis of the lumiketone and hydrocarbons assumed to be cyclopentadiene dimers, two new products.

The major new product was shown by elemental and mass spectrometric analysis to be a 1 : 1 adduct of dienone and cyclopentadiene. The presence of only nine signals in the ^{13}C n.m.r. spectrum and the simplicity of ^{1}H n.m.r. spectrum implied an element of symmetry in the molecule. The u.v. and i.r. spectra imply a strained, unconjugated carbonyl group, and taken together with the ^{1}H n.m.r. spectrum show the gross structure to be of the type (9).

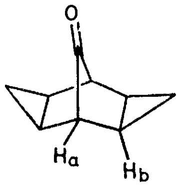
The minor new product was also shown to be a 1 : 1 adduct from its mass spectrum. It was not isolated in sufficient quantities for measurement of its ^{13}C n.m.r. spectrum but the similarities of its other spectroscopic data to those of the major adduct suggests the same gross structure.



(9)



(10)



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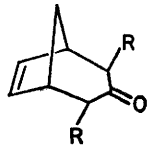
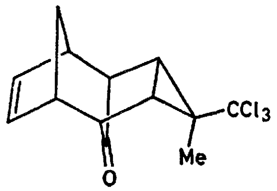
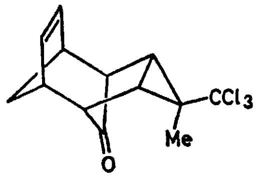


(12)

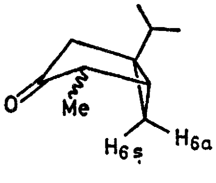
a, R = Me
b, R = CHMe$_2$
c, R,R = [CH$_2$]$_4$



(13a)



(13b)



(14)

The stereochemistry of the adducts was assigned on the basis of the n.m.r. spectra with the aid of Eu(fod)$_3$- induced shifts (see Table).

For both adducts, $J_{1,9} = J_{6,7} = 0$, suggesting that the cyclopropane is *syn* to the carbonyl group. This is consistent with a number of *endo*-tricyclo-octane derivatives (10) for which J_{ab} falls in the range 4.2—4.7 Hz[19] whereas in *exo,exo*-tetracyclononanone (11), $J_{ab} = 0$.[20]

In the major and minor adducts, $J_{12} = 5.6$ and 8.2 Hz respectively. Examination of Dreiding models of (9) with stereochemistry as in (13a and b) reveals that the dihedral angles $\theta_{1,2}$ are 35 and 0°, respectively, for which the Karplus equation predicts $J_{1,2} = 5.5$ and 8.5 Hz, respectively. Thus the major adduct has stereochemistry (13a) and the minor is (13b). Several chemical-shift differences between the adducts can be accounted for on this basis, providing supportive evidence.

Both 11-protons are at higher field in the minor isomer as expected for stereochemistry (13b) in which they lie in the shielding zone of the carbonyl group. The *syn*-proton is more affected because it is closer to the carbonyl.

^{1}H Chemical shifts [a] and Eu(fod)$_3$-induced shifts of the cyclopentadiene adducts

	Major adduct		Minor adduct		
Position	δ	Shift [b]	δ	Shift [b]	$\Delta\delta$ [c]
1,6	2.51	4.52	2.66	3.59	+0.15
2,5	2.97	1.85	3.09	1.42	+0.12
3,4	6.17	1.91	6.49	0.93	+0.32
7,9	2.20	1.78	1.84	1.42	−0.36
8-Me	1.49	2.48	1.48	2.51	−0.01
11a [d]	1.59	1.63	1.37	1.07	−0.22
11s [d]	2.74	1.85	1.66	4.00	−1.08

[a] In CDCl$_3$. [b] In p.p.m. per mole/mole ratio. [c] $\delta_{\text{minor}} - \delta_{\text{major}}$. [d] *syn* and *anti* refer to the relationship between the proton and the carbonyl group, not the double bond as is conventional in norbornene derivatives.

The vinyl protons (3-, 4-H) are at higher field in the major isomer as expected for stereochemistry (13a) in which they lie in the shielding zone of the carbonyl group [*cf.* the isomers of (12c)[21] for which a similar shift difference is observed].

The cyclopropyl protons (7-, 9-H) are at higher field in the minor isomer as expected for stereochemistry (13b) in which they lie in the shielding zone of the double bond.

Noyori *et al.*[21] have suggested that the ratio of the lanthanide-induced shifts of the *syn*- and *anti*-methylene bridge protons in the compounds (12) is diagnostic of the conformation of the six-membered ring. In a boat conformation [*cf.* (13b)] the lanthanide ion is near the bridge protons which should experience strongly differential shifting, with the *syn*-proton more affected, whereas in a chair conformation [*cf.* (13a)] the lanthanide ion is more distant and the shifting, especially of the *syn*-proton should be less. For the major and minor isomers the *syn*/*anti* induced shift ratios are 1.14 and 3.74, respectively, again consistent with the above assignment.

On this basis the stereochemistry can be confidently assigned as type (13a) for the major isomer and type (13b) for the minor. This only leaves unsettled the question of the relative orientations of the methyl and trichloromethyl groups on the cyclopropane ring, which are assigned on the basis of the europium-shifted ^{13}C n.m.r. spectrum of the major isomer. The two nuclei in question are sufficiently isolated from the site of co-ordination for the contact and co-ordination contributions to the induced shift to be negligible[22] and for the pseudocontact shift represented by $(3\cos^2\theta - 1)r^{-3}$ to be dominant. Examination of Dreiding models shows that for reasonable O–Eu distances and geometries[23] the angular parts of that expression are very similar for the two nuclei in question. Thus the induced shifts should be dominated by the radial term and the *endo*-group should be more strongly shifted.

The signals due to the methyl and trichloromethyl carbon atoms were assigned unambiguously on the basis of their chemical shifts and multiplicity on off-resonance decoupling. The europium-induced shift of the former was 4.25 times that of the latter implying that the methyl group is *endo* and that the major isomer has structure (13a).

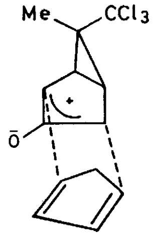
A similar approach was not possible for the minor isomer of which insufficient quantities were isolated for ^{13}C n.m.r. studies. However the closeness of the ^{1}H chemical shifts of the methyl groups (δ 1.48 and 1.49) of the two adducts suggests that both are *endo* since in both (13a and b) an *endo*-methyl group would be in the shielding zone of the carbonyl group, whereas an *exo*-methyl group would be less affected. The substantial effect of the carbonyl group can be seen in the difference between the chemical shifts of the vinyl and bridge protons of the two adducts and in the spectra of the thujones (14)[24] which have a pseudoboat conformation similar to (13a and b) and in which the 6s and 6a protons show very different chemical shifts. The minor adduct is thus assigned structure (13b).

In some runs, a third adduct was obtained in low yield (<1%) whose spectroscopic properties were consistent with its being an adduct of the type B zwitterion, *i.e.* (6b).

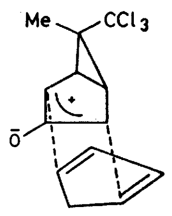
DISCUSSION

First, a 3,5-bonded intermediate is indeed formed on irradiation of a cyclohexadienone and can be trapped by dienes. Secondly the trapping occurs by 1,4-addition to the diene and 1,2-adducts were not detected. This exclusivity is characteristic of a zwitterionic species and contrasts with the results of Berson *et al.*[25] for trimethylenemethanes.

Thirdly the direction of approach of the addends is as would be predicted on the basis of work on oxyallyl systems.[26] Both cyclopentadiene adducts have the carbonyl group *syn* to the cyclopropane, implying approach of the diene to the less hindered face of the zwitterion. The major adduct has the double bond and carbonyl group *syn*, implying approach as in (15) which in Hoffmann's terminology[26] is a compact transition state whereas the minor adduct is formed *via* an extended transition state (16). This preference for the compact transition state is expected as is the greater selectivity of the furan reaction.



(15)



(16)

Fourthly, the relative orientation of the methyl and trichloromethyl groups in the adducts must reflect the stereochemistry of the zwitterion. Schuster[10] has shown that the lumiketone has an *endo*-methyl group, thus the walk process goes with inversion of configuration. This result is the same as that found by Zimmerman[7] when the ground state zwitterion is generated independently, further confirming the ground state zwitterionic character of the intermediate in the photochemical process as originally postulated.[3]

EXPERIMENTAL

^{1}H N.m.r. spectra were measured using Perkin-Elmer R12 (60 MHz) or R34 (220 MHz) or Brüker WH 90 (90 MHz) instruments. ^{13}C N.m.r. spectra were measured using the WH 90 spectrometer and are expressed as chemical shifts (multiplicity on off-resonance decoupling). I.r. and u.v. spectra were measured using Perkin-Elmer 257 and 552 instruments. Mass spectra were measured using AEI MS9 or Kratos MS80 instruments. P.l.c. was carried out on Merck Kieselgel PF 254. Bands are recorded in order of decreasing R_F. Petrol refers to light petroleum (b.p. 30—40°). Recrystallisation was from light petroleum (b.p. 60—80°). M.p.s. were measured on a Kofler hot-block and are uncorrected. Eu(fod)$_3$ was purchased from Aldrich; weighed portions of the solid were added directly to solutions in the n.m.r. tube. Unless otherwise stated, irradiations were carried out in a Rayonet-type photochemical reactor fitted with blacklight lamps emitting *ca.* 350 nm.

Irradiation of 4,4-*Dimethylcyclohexa*-2,5-*dienone* (1b) *in Furan.*—4,4-Dimethylcyclohexa-2,5-dienone (1b) (0.427 g) in furan (70 ml) was irradiated in an immersion well apparatus fitted with a 125 W medium pressure mercury lamp for 1.5 h. The solution was concentrated *in vacuo* to afford a yellow solid (537 mg), m.p. 108—120°, which was triturated with petrol and recrystallised to give 9,9-*dimethyl*-11-*oxatricyclo*[4.3.1.1^{2,5}]*undeca*-3,7-*dien*-10-*one* (6a), m.p. 124.5—125.5 °C; $\lambda_{max.}$ (MeOH) 279 nm (ε 25) and end absorption only; $\nu_{max.}$ (CHCl$_3$) 1 725s cm^{-1}; δ_H(CCl$_4$) 6.33 (1 H, dd, *J* 6.0, 1.6 Hz, 4-H), 6.25 (1 H, dd, *J* 6.0, 1.6 Hz, 3-H), 5.63 (2 H, m, 7-, 8-H), 4.93 (1 H, dd, *J* 2.4, 1.6 Hz, 2-H), 4.61 (1 H, dd, *J* 2.4, 1.6 Hz, 5-H), 2.68 (1 H, m, >9 lines, 6-H), 2.07 (1 H, t, broadened by further coupling, *J ca.* 2 Hz, 1-H), 1.33 (3 H, s, Me), and 1.06 (3 H, s, Me); δ_C(CDCl$_3$) 208.5 (s), 143.3 (d), 134.2 (d), 121.6 (d), 80.3 (d), 62.3 (d), 53.9 (d), 42.1 (s), 29.2 (q), and 25.7 p.p.m. (q); *m/e* 190 (100%), 175 (30), and 147 (35) (Found: C, 75.7; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.75; H, 7.4%). P.l.c. of the mother-liquors (ether–petrol 1 : 9, ×2) afforded further adduct and a trace of 6,6-dimethylcyclohexa-2,4-dienone.

Irradiation of 4-*Methyl*-4-*trichloromethylcyclohexa*-2,5-*dienone* (1c) *in Furan.*—The dienone (82 mg) in furan (2 ml) was irradiated for 20 h. The solution was concentrated *in vacuo* and subjected to p.l.c. (1 : 9 ether–petrol, ×4). Band 1 was 2-(2-*furyl*)-6-*methyl*-6-*trichloromethylbicyclo*[3.1.0]-*hexan*-3-*one* (7), $\nu_{max.}$ (CHCl$_3$) 1 745s cm^{-1}; δ_H(CCl$_4$) 7.33 (1 H, dd, *J* 1.7, 0.9 Hz, 5′-H), 6.28 (1 H, dd, *J* 3.2, 1.7 Hz, 4′-H), 6.14 (1 H, dt, *J* 3.2, 0.9 Hz, 3′-H), 3.42br (1 H, s, $W_{\frac{1}{2}}$ 2.6 Hz, 2-H), 2.81 (1 H, dt, *J* 19.8, 0.9 Hz, 4-H), 2.48 (2 H, m, 1-, 5-H), 2.34 (1 H, d, *J* 19.8 Hz, 4-H), and 1.43 (3 H, s, Me); δ_H(C$_6$D$_6$) 7.03 (1 H, dd, *J* 1.7, 0.9 Hz, 5′-H), 6.04 (1 H, dd, *J* 3.2, 1.7 Hz, 4′-H), 5.97 (1 H, dt, *J* 3.2, 0.9 Hz, 3′-H), 3.23 (1 H, s, 2-H), 2.37 (1 H, d, *J* 8.6 Hz, 1-H), 2.27 (1 H, ddd, *J* 19.8, 7.0, 1.1 Hz, 4-H) 1.99 (1 H, dd, *J* 8.6, 7.0 Hz, 5-H), 1.84 (1 H, d, *J* 19.8 Hz, 4-H), and 1.03 (3 H, s, Me) (Found: M^+, 291.980 6. $C_{12}H_{11}O_2{}^{35}Cl_3$ requires M^+, 291.982 5). Band 2 was starting dienone.

Irradiation of 4-*Methyl*-4-*trichloromethylcyclohexa*-2,5-*dienone* (1c) *in Furan containing Triethylamine.*—The dienone (100 mg) and triethylamine (10 mg) in furan (2 ml) were irradiated for 4 h. The solution was concentrated *in vacuo* and treated with carbon tetrachloride to afford a solid, assumed to be triethylamine hydrochloride and a brown solution, the n.m.r. spectrum of which showed signals at δ 6.25 (2 H, s), 4.82 (2 H, d, *J* 3.5 Hz), 2.58 (2 H, d, *J* 3.5 Hz), 2.33 (2 H, s), and 1.49 (3 H, s) in addition to those due to unchanged starting material and a trace of *p*-cresol.

Irradiation of 4-*Methyl*-4-*trichloromethylcyclohexa*-2,5-*dienone* (1c) *in the Presence of Cyclopentadiene.*—The dienone (1.00 g) in benzene containing 10% (v/v) freshly distilled cyclopentadiene (80 ml) was irradiated for 25 h. The solution was concentrated *in vacuo* (rotary evaporator, then 0.01 mmHg) to afford an orange oil (1.64 g) which was subjected to p.l.c. (1 : 19 ether–petrol, ×4). Band 1 (323 mg) was crystallised from petrol and recrystallised to afford syn-8-*methyl*-8-*trichloromethyltetracyclo*[4.3.1.1^{2,5}.0^{7,9}]*undeca*-3-*en*-10-*one* (13b), m.p. 108—111 °C; $\lambda_{max.}$ (MeOH) 284 nm (ε 24) and end absorption only; $\nu_{max.}$ 1 740s cm^{-1}; δ_H(CCl$_4$) 6.48br (2 H, s, 3-, 4-H), 3.09 (2 H, d, each branch further split >8 lines, *J ca.* 8 Hz, 2-, 5-H), 2.59 (2 H, d, *J* 8.2 Hz, 1-, 6-H), 1.81 (2 H, s, 7-, 9-H), 1.67 (1 H, dtt, *J* 11.1, 1.1, 1.0 Hz, 11s-H), 1.47 (3 H, s, Me), and 1.39 (1 H, dt, *J* 11.1, 3.3 Hz, 11a-H); *m/e* 290 (0.1%), 255 (61), and 66 (100) (Found: M^+, 290.003 0. $C_{13}H_{13}O^{35}Cl_3$ requires M^+, 290.003 2). Band 2 (361 mg) was treated similarly to afford the anti-*isomer* (13a), m.p. 133—135 °C; $\lambda_{max.}$ (MeOH) 280sh nm (ε 23) and end absorption only; $\nu_{max.}$ (CHCl$_3$) 1 753s cm^{-1}; δ_H(CCl$_4$) 6.13br (2 H, t, *J* 1.7 Hz, 3-, 4-H), 2.95br (2 H, s, $W_{\frac{1}{2}}$ 12 Hz, 2-, 5-H), 2.74 (1 H, dt, *J* 10.8, 1.3 Hz, 11s-H), 2.42 (2 H, d, *J* 5.5 Hz, 1-, 6-H), 2.15 (2 H, s, 7-, 9-H), 1.56 (1 H, dt, *J* 10.8, 3.1 Hz, 11a-H), and 1.47 (3 H, s, Me); δ_C(CDCl$_3$) 212.5 (s), 137.5 (d), 106.2 (s), 51.9 (d), 47.6 (d), 44.6 (s), 39.5 (d), 32.0 (q), and 13.5 (t); *m/e* 290 (0.1%) and 255 (100) (Found: C, 53.9; H, 4.5; Cl, 35.9. $C_{13}H_{13}Cl_3O$ requires C, 53.55; H, 4.5; Cl, 36.45%). Band 3 (281 mg) contained starting dienone and a trace of *p*-cresol. Band 4 (140 mg) was resubjected to p.l.c. (1 : 9 ether–petrol, ×4). Band 4a (9 mg) crystallised on standing and was triturated with petrol to afford 9-*methyl*-9-*trichloromethyltricyclo*[4.3.1.1^{2,5}]*undeca*-3,7-*dien*-10-*one* (6b), m.p. 139—146 °C; $\nu_{max.}$ (CHCl$_3$) 1 735s cm^{-1}; δ(CDCl$_3$) 6.27 (1 H, ddd, *J* 5.5, 2.8, 1.1 Hz), 6.12 (2 H, m), 6.05 (1 H, ddd, *J* 5.5, 2.8, 1.1 Hz), 3.07 (1 H, m), 2.95 (2 H, m), 2.88 (1 H, m), 2.59 (1 H, d, *J* 11.3 Hz), and 1.73 (3 H, s) partially obscuring 1.72 (1 H, dt, *J* 11.3, 3.6 Hz); *m/e* 290 (2%) and 173 (100) (Found: M^+, 289.999 9. $C_{13}H_{13}{}^{35}Cl_3O$ requires M^+, 290.003 2). Band 4b contained the methyltrichloromethylbicyclo[3.2.0]heptenone previously reported.[18]

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