Dichloroketen Adducts of 6,6-Diphenylfulvene and 8,8-Diphenylbenzofulvene[1]

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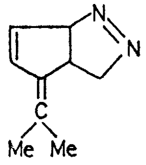
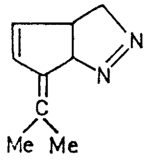
The reaction of dichloroketen with 6,6-diphenylfulvene afforded a crystalline cycloadduct identified as *cis*-7,7-dichloro-4-diphenylmethylenebicyclo[3,2,0]hept-2-en-6-one by n.m.r. and chemical degradation studies. Similarly, the adduct obtained from dichloroketen and 8,8-diphenylbenzofulvene was shown to be *cis*-2,2-dichloro-2,2a,7,7a-tetrahydro-7-diphenylmethylene-1*H*-cyclobut[*a*]inden-1-one by n.m.r. analysis.

THE addition of ketenes to conjugated dienes generally yields 1,2-adducts. The formation of 1,4-adducts has not hitherto been observed.[2] Depending on the conditions, the reaction can proceed *via* diradical,[3] ionic,[2] or concerted mechanisms.[4]

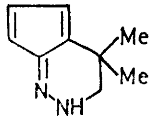
Fulvenes react with dienophiles to produce Diels–Alder type 1,4-adducts.[5] The formation of 1,2-monoadducts is unusual. In 1961 Alder and his co-workers[6] reported that the addition of 1 mol. equiv. of diazomethane to dimethylfulvene yielded an adduct whose structure could be either (1) or (2). Recently, Houk and Luskus[7] proved by n.m.r. analysis that the compound had in fact structure (3). In two other instances the formation of 1,2-monoadducts of fulvenes has been postulated.[8]



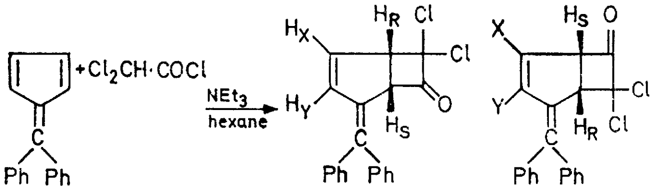
(1)



(2)



(3)



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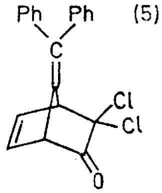

(6)

We report here the structures of the adducts formed from reactions of dichloroketen with 6,6-diphenylfulvene and 8,8-diphenylbenzofulvene.[1]

Reaction of Dichloroketen with 6,6-*Diphenylfulvene*.—The reaction of dichloroketen (generated *in situ*)[9] with 6,6-diphenylfulvene afforded a crystalline product in 55% yield, for which structures (4)—(6) were all possible on the assumption of *cis*-cycloaddition. Structure (6) was ruled out on the basis of the observed i.r. carbonyl absorption at 1810 cm^{-1}, which is reasonable for a saturated four-membered ring.[10] To distinguish between structures (4) and (5) the n.m.r. spectrum of the adduct in deuteriochloroform was studied (Table 1).

TABLE 1

N.m.r. data for compound (4)

δ/p.p.m.	Number of protons	Multiplicity	Coupling constant (Hz)	Assignment
7·06—7·50	10	m		
6·52	1	dd	J_{YX} 5·7 J_{YR} −1·8	H_Y
6·02	1	ddd	J_{XY} 5·7 J_{XR} 2·9 J_{XS} 0·9	H_X
4·73	1	dd	J_{SR} 6·6 J_{SX} 0·9	H_S
4·2	1	ddd	J_{RS} 6·6 J_{RX} 2·9 J_{RY} −1·8	H_R

The splitting patterns were analysed by construction methods[11] and the first-order results are shown in the coupling diagram (Figure 1). The proton assignments fit perfectly for the structure (4). Structure (5) would require a long-range coupling J_{RX} of ±2·9 Hz, which is too large for this four-bond system. The observed coupling J_{SX} of 0·9 Hz was considered reasonable for the four-bond system in structure (4). This is also in good agreement with the bond angles (ϕ_1 120, ϕ_3 0°) observed in a Dreiding model of structure (4) if the Barfield relationship[12] for saturated systems is used as an

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[1] Preliminary communication, R. E. Harmon, W. D. Barta, S. K. Gupta, and G. Slomp, *Chem. Comm.*, 1970, 935.

[2] R. Huisgen and R. Otto, *Tetrahedron Letters*, 1968, **3**, 4491.

[3] J. D. Roberts and C. M. Sharts, *Org. Reactions*, 1962, **12**, 26.

[4] W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, 1967, **32**, 612.

[5] R. B. Woodward and H. Baer, *J. Amer. Chem. Soc.*, 1944, **66**, 645; K. Alder, F. W. Chambers, and W. Trimborn, *Annalen*, 1950, **566**, 27.

[6] K. Alder, R. Braden, and F. H. Flock, *Chem. Ber.*, 1961, **94**, 456.

[7] K. N. Houk and L. J. Luskus, *Tetrahedron Letters*, 1970, 4029.

[8] (*a*) A. Quilico, P. Grunager, and R. Mazzini, *Gazzetta*, 1952, **82**, 349 (*Chem. Abs.*, 1954, **48**, 2039d); (*b*) H. Paul, I. Lange, and A. Kausmann, *Z. Chem.*, 1963, **3**, 61 (*Chem. Abs.*, 1963, **57**, 5146d).

[9] T. R. Potts and R. E. Harmon, *J. Org. Chem.*, 1969, **34**, 2792.

[10] J. M. Conia and J. L. Ripoll, *Bull. Soc. chim. France*, 1963, 768.

[11] G. Slomp, *Appl. Spectroscopy*, 1969, **3**, 263.

[12] M. Barfield, *J. Chem. Phys.*, 1964, **41**, 3825.

approximation ($J_{\text{calc.}}$ +0·6 Hz). The four-bond coupling J_{RY} of −1·8 Hz was in excellent agreement with that calculated from the bond angles (*trans*, ϕ 30°) by use of the Barfield relationship[12] for allylic systems ($J_{\text{calc.}}$ −1·75 Hz).

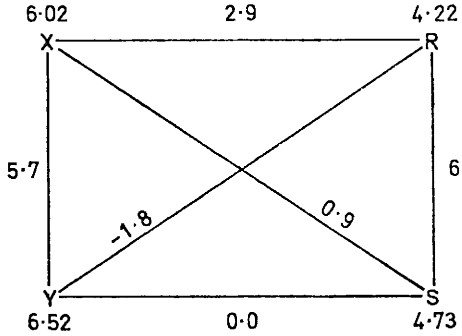
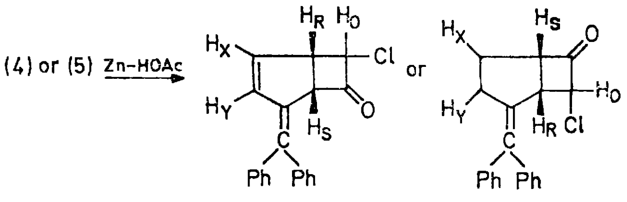


FIGURE 1 Coupling diagram for compound (4)

Treatment of the adduct with zinc dust and acetic acid yielded a crystalline product in 57% yield. On the basis of elemental analysis and i.r. data [$\nu_{\text{max.}}$ 1795 (C=O), 1465 (aromatic), 701 and 748 (C–Cl) cm^{-1}] this could have the structure (7) or (8). As before, the distinction between these two structures was made by n.m.r. spectroscopy (Table 2). The splitting patterns were analysed by construction methods[11] and the results are shown in the coupling diagram (Figure 2). The couplings in the ORS system, including the long-range OS coupling were consistent with the all-*cis*-structure (7).



(7) (8)

TABLE 2

N.m.r. data for compound (7)

δ/p.p.m.	Number of protons	Multiplicity	Coupling constants (Hz)	Assignment
7·08—7·51	10	m		
6·48	1	ddd	J_{YX} 6·0 J_{YR} 1·5 J_{YX} 0·5	H_{Y}
6·09	1	ddd	J_{XY} 6·0 J_{XR} 2·5 J_{XS} 1·0	H_{X}
5·07	1	ddd	J_{OR} 9·0 J_{OS} 3·0	H_{O}
4·36	1	ddd	J_{SR} 7·0 J_{SO} 3·0 J_{SY} 1·0 J_{SX} 0	H_{S}
4·08	1	Partly overlapping ddd	J_{RO} 9·0 J_{RS} 7·0 J_{RX} 2·5 J_{RY} 1·5	H_{R}

Chemical Degradation of the Adduct (4).—The key step in our degradation scheme was the ring-cleavage reaction. Ghosez *et al.*[13] degraded the adduct (9) with sodium methoxide to give the cyclopentene derivative (10). However, when this reaction was performed on the adduct (4), it led to considerable decomposition, which prevented the isolation of any product. We therefore first removed the chlorine atoms in (4) by treatment with zinc and acetic acid. The resulting compound, 4-diphenylmethylenebicyclo[3,2,0]hept-2-ene-6-one (11), was cleaved by sodium methoxide to give a 67% yield of methyl (4-diphenylmethylenecyclopent-2-enyl)acetate (12). The endocyclic double bond in compound (12) was selectively reduced over 10% palladium–charcoal to give compound (13) in 85% yield. Oxidation of the exocyclic double bond in (13) was then attempted.

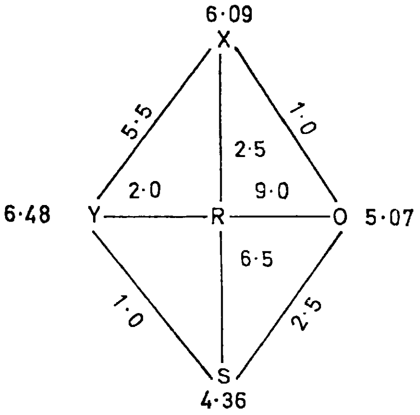
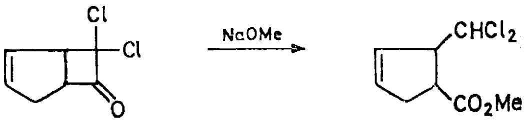
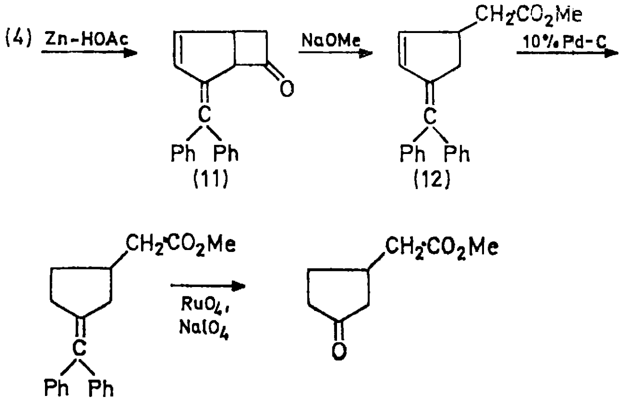


FIGURE 2 Coupling diagram for compound (7)



(9) (10)



(13) (14)

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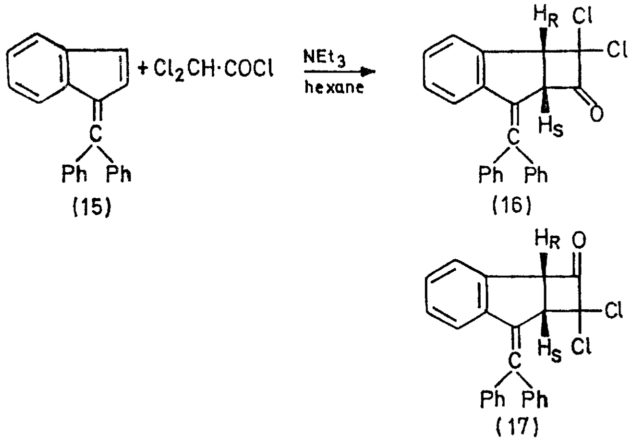
[13] L. Ghosez, R. Montaigne, and P. Mollett, *Tetrahedron Letters*, 1966, **1**, 135.

Potassium permanganate and sodium periodate[14] were unsatisfactory as oxidants, but use of a combination of ruthenium tetroxide and sodium periodate gave methyl (3-oxocyclopentyl)acetate (14), isolated as its 2,4-dinitrophenylhydrazone which was identical with an authentic sample prepared according to literature procedures.[15,16]



(15) (16) (17)

Reaction of Dichloroketen with 8,8-*Diphenylbenzofulvene* (15).—As in diphenylfulvene, the exocyclic double bond in benzofulvenes is very unreactive, and because of the availability of only one ring double bond, the usual 1,4-cycloaddition is not possible. According to Bergmann,[17] benzofulvenes seem to be unreactive towards dienophiles. The reaction of dichloroketen with 8,8-diphenylbenzofulvene (15) yielded a crystalline adduct which could have structure (16) or (17) on the assumption of a *cis*-cycloaddition. Its i.r. spectrum, showing strong bands at 1800 (C=O), 1600, 1450 (aromatic), 795, 775, and 700 (C–Cl) cm^{-1}, was consistent with either structure, and n.m.r. spectroscopy did not permit an unambiguous assignment. The adduct was therefore hydrogenated over 5% palladium–barium sulphate to give a crystalline compound which on the basis of elemental analysis and mass spectral data (M^+ 358 and 360 with intensities appropriate for one chlorine atom) could have structure (18) or (19). Its i.r. spectrum showed a strong carbonyl peak at 1785 cm^{-1}. The n.m.r. spectrum is shown in Figure 3. The splitting patterns were analysed by construction methods[11] and the results are included. The observed coupling J_{SQ} of 7·7 Hz indicated that the H_S and H_Q must be vicinal. The PQS sub-spectrum was recognized as a deceptively simple ABX type in which one of the P-energy levels corresponded exactly to one of the Q-energy levels.[11] Thus, the eight-line pattern normally seen in the AB part had collapsed to five lines, one AB quartet and a degenerate singlet. Since the singlet was situated between the A and B shifts of the AB quartet, it illustrated an example of the rare type of deceptive situation where

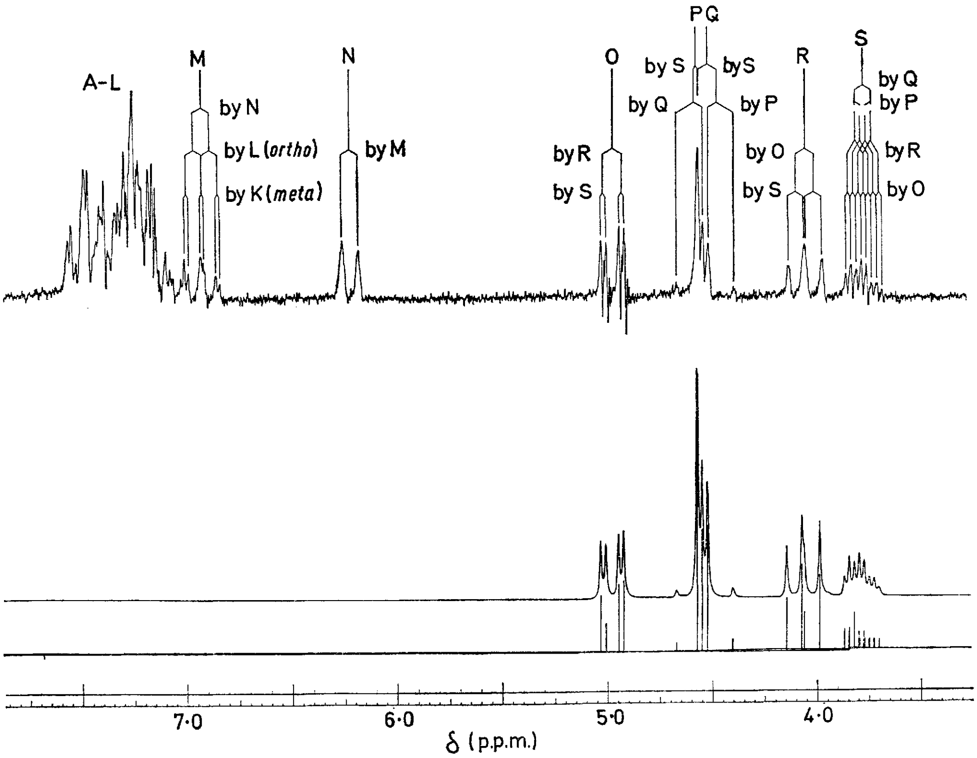


FIGURE 3 N.m.r. spectrum of compound (18) (100 MHz) and computer-calculated spectrum (LAOCN-3)

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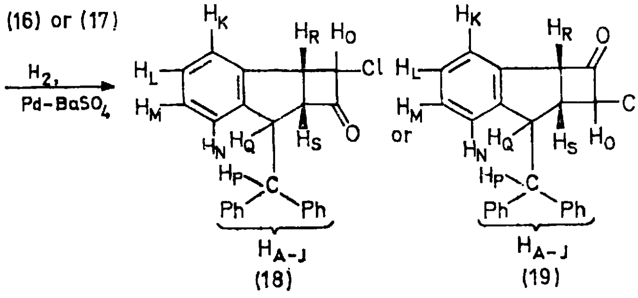
[14] R. U. Lemieux and E. VonRudolff, *Canad. J. Chem.*, 1955, **33**, 1701.

[15] E. J. Forbes and R. A. Ripley, *Chem. and Ind.*, 1960, 589.

[16] J. Meinwald and E. Frauenglass, *J. Amer. Chem. Soc.*, 1960, **82**, 5235.

[17] E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 65.

AX and BX couplings have unlike signs (a computed example of such a case is recorded in Figure 28 of ref. 11). The coupling J_{PS} was given a negative sign since it was much smaller than the coupling J_{QS}. The H_S multiplet was analysed as two first-order perturbations on the X-pattern as expected from the treatment of PQ as an ABX system.



The foregoing analysis of the OPQRS system was confirmed and refined by computer (LAOCN-3 program [11]). The results are shown in Table 3. The long-range couplings J_{OP}, J_{OQ}, and J_{PR} were held at zero. The computer found a long-range coupling J_{QR} of —0·15 Hz, which explained the broadening of the H_Q and H_R signals. The resulting coupling diagram is shown in Figure 4.

TABLE 3

Computer analysis of the OPQRS portion of the n.m.r. spectrum of (18)

Proton	δ/p.p.m.	Coupling	J/Hz
O	4·96612	OP	0
P	4·56609	OQ	0
Q	4·52081	OR	8·671
R	4·04953	OS	2·321
S	3·77501	PQ	12·272
		PR	0
		PS	−0·443
		QR	−0·149
		QS	7·647
		RS	7·414

R.m.s. error of fit = 0·310.

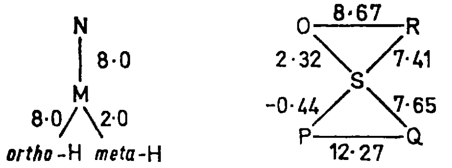


FIGURE 4 Coupling diagram of compound (18) from computer analysis

From the foregoing analysis of the n.m.r. spectrum, the structure (18) appears to be more reasonable than (19). The chemical shifts and the magnitude of the long-range couplings render the structure (19) unlikely. Although the chemical shifts of tertiary hydrogen atoms are susceptible to anisotropy effects, the observed shifts of H_R and H_S seem more satisfactory for (18) than for (19). Furthermore, it seemed more reasonable to consider the small coupling J_{OS} (2·3 Hz) as the long-range coupling, as in (18), than to consider the large coupling J_{OR} (8·7 Hz) as the long-range coupling as required by structure (19).

The observed coupling in (18) indicated an all-*cis*-relationship for the substituents on the five-membered ring. These values of the long-range couplings agreed well with the values calculated on the basis of Barfield's theory,[12] which relates couplings to the bond angles. The hydrogen atoms H_R and H_Q in a Dreiding model of (18) showed bond angles of about 60° with reference to the three-carbon atom plane ($J_{calc.}$ —0·1 Hz, $J_{obs.}$ —0·15 Hz). The coupling J_{PS} (—0·43 Hz) seemed reasonable when the diphenylmethyl group was rotated to place H_P *trans* to H_Q. The vicinal coupling J_{PQ} of 12·3 Hz was also in agreement with the *trans*-rotamer. Thus, the structure of the hydrogenation product of the adduct is established as (18), and that of the original adduct must be (16) and not (17).

EXPERIMENTAL

M.p.s were taken with a Thomas–Hoover Unimelt apparatus. A Beckman IR-8 spectrophotometer was used to determine the i.r. spectra. The n.m.r. spectra were obtained with 60 and 100 MHz Varian spectrometers (deuteriochloroform as solvent and tetramethylsilane as internal standard). The elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana. Diphenylfulvene was prepared by treating a solution of cyclopentadiene in sodium ethoxide with benzophenone.[18] Similarly, diphenylbenzofulvene (15) was prepared from indene and benzophenone.[19]

cis-7,7-*Dichloro-4-diphenylmethylenebicyclo*[3,2,0]*hept-2-en-6-one* (4).—A solution of dichloroacetyl chloride (25·7 g, 0·174 mol) in anhydrous hexane (20 ml) was added dropwise to a hot solution of 6,6-diphenylfulvene (40·0 g, 0·174 nol) and freshly distilled triethylamine (19·3 g, 0·190 mol) in anhydrous hexane (800 ml) during 40 min, and the mixture was refluxed for 4 h. More dichloroacetyl chloride (25·7 g, 0·174 mol) and triethylamine (19·3 g, 0·190 mol) were then added. Refluxing was continued for 4 h and then the mixture was cooled in an ice-bath. The solid was filtered off and washed with ether. The ether–hexane solution was washed in succession with water, 5% sodium hydrogen carbonate solution, and saturated sodium chloride solution, dried ($MgSO_4$), and evaporated to leave a tan solid. Three recrystallizations from acetone–water gave *compound* (4), m.p. 137·5—138°, $\nu_{max.}$ (Nujol) 1804 (C=O), 778, 767, 753, 726, and 707 (Ar and/or C–Cl), and 692 and 648 (C–Cl) cm^{-1}, δ ($CDCl_3$) 7·28 (10H, m, ArH), 6·52 (1H, m, C*H*=CH), 6·02 (1H, m, CH=C*H*), 4·73 (1H, m, CH–C=O), and 4·22 p.p.m. (1H, m, CH·CCl) (Found: C, 70·7; H, 3·7; Cl, 20·75. $C_{20}H_{14}Cl_2O$ requires C, 70·4, H, 4·15; Cl, 20·8%).

4-*Diphenylmethylenebicyclo*[3,2,0]*hept-2-en-6-one* (11).—A slurry of compound (4) (12·8 g, 0·0378 mol), powdered zinc (12·3 g, 0·189 mol), methanol (80 ml), and glacial acetic acid (80 ml) was refluxed for 4 h. The mixture was filtered hot and the filtrate was cooled in the refrigerator. Filtration gave *needles* (8·6 g, 84%), m.p. 125—126° (from hot methanol), $\nu_{max.}$ (Nujol) 1765 (C=O), 1585 and 1560 (C=C), and 773, 752, and 700 (Ar) cm^{-1}, $\lambda_{max.}$ (95% EtOH) 280

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[18] J. Thiele, *Ber.*, 1900, **33**, 666.

[19] J. Thiele and E. Marck, *Annalen*, 1918, **415**, 257.

nm (ε 2·1 × 10^6), δ ($CDCl_3$) 7·33 (10H, m, ArH), 6·38 (1H, d, C*H*=CH), 6·15 (1H, m, CH=C*H*), 4·49 (1H, m, CH·C=O), 3·69 (1H, m, C*H*·CH_2), and 2·92 p.p.m. (2H, m, CH_2) (Found: C, 88·0; H, 6·0; O, 6·1. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9; O, 5·85%).

Methyl (4-*Diphenylmethylenecyclopent*-2-*enyl*)*acetate* (12).—A solution of sodium methoxide (1·0 g, 0·018 mol) in anhydrous methanol (10 ml) was added dropwise to a solution of compound (11) (4·0 g, 0·015 mol) in anhydrous tetrahydrofuran (40 ml) at −10° under nitrogen during 20 min. The solution was stirred for 1 h at −10°, then allowed to warm to 0°, and acidified to pH 4 with glacial acetic acid. It was diluted with an equal amount of water and extracted with methylene chloride. The extract was washed in succession with water, 5% sodium hydrogen carbonate solution, and saturated sodium chloride solution, dried (Na_2SO_4), and evaporated to yield yellow oil which was chromatographed over silica gel (475 g). Elution with benzene yielded *compound* (12) (3·7 g, 67%), which was unstable in the presence of air and could be isolated only in about 95% purity; $\nu_{max.}$ (neat) 1600 and 1575 (C=C), 2955, 2925, 2855, 1460, and 1380 (alkane), 1725 (CO_2Me), 1275, 1122, 1072, and 1040 (OMe), and 741 and 704 (Ar) cm^{-1}, $\lambda_{max.}$ (95% EtOH) 280 nm (ε 2·6 × 10^5), δ ($CDCl_3$) 7·19 (10H, s, ArH), 6·25 (2H, m, CH·CH), 3·61 (3H, s, OMe), and 3·39—2·13 p.p.m. (5H, m, CH_2·CH·CH_2) (Found: C, 81·3; H, 6·6. $C_{21}H_{20}O_2$ requires C, 82·85; H, 6·65%).

Methyl (3-*Diphenylmethylenecyclopentyl*)*acetate* (13).—A slurry of freshly prepared compound (12) (2·0 g, 0·0069 mol) and 10% palladium–charcoal (0·167 g) in ethyl acetate (30 ml) was hydrogenated at atmospheric pressure (uptake 170 ml in 1 h; calc. 155 ml). Filtration and evaporation left an oil which was chromatographed on silica gel (170 g). Elution with 5 : 1 benzene–chloroform gave *compound* (13) (1·8 g, 85%), which was also unstable in air; $\nu_{max.}$ (neat) 1600 (C=C), 3010, 1490, 757, 746, and 700 (Ar), 2950 and 1440 (alkane), and 1255, 1200, 1170, and 1030 (OMe) cm^{-1}, δ ($CDCl_3$) 7·23 (10H, s, ArH), 3·62 (3H, s, OMe), and 2·32 p.p.m. (9H, m, CH_2 and CH) (Found: C, 81·45; H, 7·6. $C_{21}H_{22}O_2$ requires C, 82·3; H, 7·25%).

Methyl (3-*Oxocyclopentyl*)*acetate* (14).—A solution of compound (13) (0·907 g, 0·00335 mol) in acetone (110 ml) was prepared. The flask was flushed with nitrogen and a mixture of freshly prepared ruthenium tetroxide [20] (0·350 g, 0·00265 mol) in carbon tetrachloride (7 ml) and sodium periodate (2·0 g, 0·0094 mol) in distilled water (50 ml) was added with stirring. The resulting mixture darkened rapidly and became warm. The flask was cooled and sodium periodate (10·0 g, 0·0467 mol) was added in 2·0 g portions as the black ruthenium dioxide precipitate was formed. After 24 h the excess of ruthenium tetroxide was destroyed with methanol (20 ml). The precipitate was filtered off and washed with acetone, and the filtrate was evaporated under reduced pressure until the organic solvents had been removed. The residual aqueous layer was extracted with ether. The extract was washed with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated under reduced pressure to yield a yellow oil, which was chromatographed over silica gel (170 g). Elution with chloroform gave compound (14) (0·350 g, 67%), i.r. spectrum nearly identical with that of an authentic sample: $\nu_{max.}$ 2950, 1440, 1405, 1375, and 1340 (alkane), 1740 (CO_2Me), 1710 (C=O), and 1200 and 1160 (OMe) cm^{-1}.

2,4-Dinitrophenylhydrazine (0·4 g) was dissolved in conc. sulphuric acid (2 ml), distilled water (3 ml), and methanol (10 ml). This solution (3 ml) was added to compound (14) (0·093 g) in methanol (2 ml). Crystallization began immediately after mixing and was allowed to proceed for 2 h. The flask was cooled in the refrigerator overnight. Filtration yielded the *dinitrophenylhydrazone*, m.p. 135—136° (from ethyl acetate) (lit.,[15] 134—135°), $\nu_{max.}$ (Nujol) 3300 (NH), 1730 (CO_2Me), 1335 ($ArNO_2$), 1500, 841, 833, 743, and 720 (Ar), 1455 and 1415 (alkane), and 1270, 1210, 1175, 1130, and 1070 (OMe) cm^{-1} (Found: C, 50·3; H, 4·8; N, 16·4. $C_{14}H_{16}N_4O_6$ requires C, 50·0; H, 4·8; N, 16·65%), identical (mixed m.p. and i.r. spectrum) with an authentic sample.

cis-7-*Chloro*-4-*diphenylmethylenebicyclo*[3,2,0]*hept*-2-*en*-6-*one* (7).—A slurry of compound (4) (32·6 g, 0·0962 mol), powdered zinc (7·1 g, 0·109 mol), methanol (100 ml), and glacial acetic acid (100 ml) was refluxed for 17 h. The mixture was filtered hot and cooled in the refrigerator. Filtration gave *compound* (7) (16·7 g, 57%), m.p. 163—164° (from hot methanol), $\nu_{max.}$ (Nujol) 1790 (C=O), 776, 762, 748, and 702 (Ar and/or C–Cl), and 666 and 638 (C–Cl) cm^{-1}, δ ($CDCl_3$) 7·30 (10H, m, ArH), 6·48 (1H, m, C*H*=CH), 6·09 (1H, m, CH=C*H*), 5·07 (1H, m, CHCl), 4·36 (1H, m, CH·C=O), and 4·08 p.p.m. (1H, m, C*H*·CHCl) (Found: C, 78·0; H, 5·2; Cl, 11·85. $C_{20}H_{15}ClO$ requires C, 78·3; H, 4·95; Cl, 11·55%).

Authentic Methyl (3-*Oxocyclopentyl*)*acetate* 2,4-*Dinitrophenylhydrazone*.—3-Oxocyclopentylacetic acid, prepared [16] from cyclopentanone and diethyl malonate, was esterified with diazomethane to yield the acetate (14) in 95% yield. The 2,4-dinitrophenylhydrazone had m.p. 135—136° (lit.,[15] 134—135°), $\nu_{max.}$ (Nujol) 3300 (NH), 1730 (CO_2Me), 1335 ($ArNO_2$), 1500, 841, 833, 743, and 720 (Ar), 1455 and 1415 (alkane), and 1270, 1210, 1175, 1130, and 1070 (OMe) cm^{-1}.

cis-2,2-*Dichloro*-2,2a,7,7a-*tetrahydro*-7-*diphenylmethylene*-1H-*cyclobut*[a]*inden*-1-*one* (16).—A solution of dichloroacetyl chloride (4·5 g, 0·03 mol) in anhydrous hexane (10 ml) was added rapidly to a hot solution of 8,8-diphenylbenzofulvene (8·2 g, 0·03 mol) and freshly distilled triethylamine (3·0 g, 0·03 mol) in anhydrous hexane (250 ml). The mixture was heated to reflux. More dichloroacetyl chloride (0·45 mol) and triethylamine (0·45 mol) were added in 0·03 mol portions during 24 h. After 80 h under reflux, the mixture was cooled in an ice-bath. The resulting solid was filtered off and washed with ether. The filtrate was evaporated and the black residue was triturated with light petroleum (b.p. 30—60°). Evaporation left a yellow solid (2·5 g, 22%), which yielded *compound* (16), m.p. 170—171° (from benzene–hexane), $\nu_{max.}$ (Nujol) 1802 (C=O), 1495, 1460, and 1447 (Ar), 794, 774, 765, 753, and 700 (Ar and/or C–Cl), and 656, 649, and 632 (C–Cl) cm^{-1}, δ ($CDCl_3$) 7·70—6·20 (14H, m, ArH), 4·96 (1H, d, ArCH), 4·46 (1H, d, ArCH), and 4·46 p.p.m. (1H, m, CH·C=O) (Found: C, 73·45; H, 4·2; Cl, 18·0. $C_{24}H_{16}Cl_2O$ requires C, 73·65; H, 4·1; Cl, 18·1%).

cis-2-*Chloro*-2,2a,7,7a-*tetrahydro*-7-*diphenylmethyl*-1H-*cyclobut*[a]*inden*-1-*one* (18).—A slurry of compound (16) (0·500 g, 0·00128 mol) and palladium–barium sulphate (0·500 g) in ethanol (50 ml) was hydrogenated at 60 lb in^{-2} at 25° for 4 h. The catalyst was filtered off and washed with chloroform. The filtrate was evaporated to dryness to yield *compound* (18) (0·450 g, 90%), m.p. 210—211°

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[20] L. M. Berkowitz and P. N. Rylander, *J. Amer. Chem. Soc.*, 1958, **80**, 6682.

[from benzene–light petroleum (b.p. 60—110°)], $\nu_{max.}$ (KBr) 1802 (C=O), 3062, 1495, 1465, and 1448 (Ar), 762, 754, 748, 741, 730, and 700 (Ar and/or C–Cl), 689 (C–Cl), and 2930 (alkane) cm^{-1}, δ (CDCl$_3$) 7·58—6·15 (14H, m, ArH), 4·97 (1H, m, CHCl), 4·57 (1H, m, ArCH), 4·52 (1H, m, ArCH), 4·05 (1H, m, CH·C=O), and 3·78 p.p.m. (1H, m, C*H*·CHCl) (Found: C, 80·25; H, 5·4; Cl, 9·95. $C_{24}H_{19}ClO$ requires C, 80·35; H, 5·35; Cl, 9·9%).

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