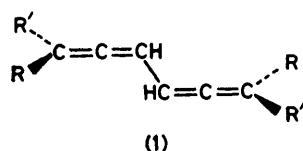


Cycloadditions to Conjugated Diallenes

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Conjugated diallenes of the general structure (1) reacted with *N*-phenyl-1,2,4-triazoline-3,5-dione (5) to give [4 + 2] cycloaddition products; the *meso*-diallene (4) with (5) gave the unsymmetrical Diels–Alder adduct (8) and the 'ene' product (9). Reaction of diallene (2) with sulphinylaniline gave the Diels–Alder product (11) while reactions with ketens resulted in both [2 + 2] and [4 + 2] cycloaddition products.

DIALLENES of the general structure (1) embrace the properties of a cumulative system as well as those of a conjugated diene; hence, both [2 + 2] and [4 + 2] cycloadditions would be expected to take place with appropriate reagents. Reactions of diallene itself with a variety of dienophiles have been reported¹ to yield [2,2]paracyclophanes; with substituted diallenes only one example of cycloaddition is known, *e.g.* the Diels–Alder adduct formed from tetramethyldiallene (2) and *N*-phenylmaleimide.² Furthermore, the addition of sulphur dioxide to a number of diallenes gave the corresponding sulpholens in high yields.³ In the present work we want to describe some results from cycloadditions of diallenes with some dienophiles and heterocumulenes with the object of learning more about the reactivity of this unique unsaturated system.

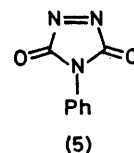


- (2) R = R' = Me
 (3) R = R' = Ph
 (4) R = Me, R = Ph

The diallenes (2), (3), and *meso*-(4) were chosen for our studies. Compounds (2) and (4) were prepared by adding dibromo-carbene to the respective conjugated diene followed by treatment of the bis-adduct with methyl-lithium;⁴ tetraphenyldiallene (3) was prepared by reduction of tetraphenylhexapentaene.⁵ In con-

nection with the preparation of the diallene (4), the addition of dibromocarbene, generated from bromoform and potassium *t*-butoxide, provided the bis-adduct in 87% yield as a 72 : 28 mixture of the *meso* and racemic forms; from previous experiments only the *meso*-adduct had been isolated. The yield of bis-adducts was reduced to 53% using the phase-transfer method for generation of dibromocarbene,⁶ and the ratio of *meso* and racemic forms was 55 : 45. These results support previous observations that dihalogenocarbenes formed under phase-transfer conditions appear less discriminating in their reactions.⁷

The three diallenes all underwent cycloaddition with the very reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (5) (PTAD) although at very different rates.



The reaction of tetramethyldiallene (2) was extremely fast as evidenced by the immediate disappearance of the red colour of PTAD; the cyclo-adduct (6) was formed in practically quantitative yield and characterized by spectroscopic evidence. On the other hand the tetraphenyldiallene (3) reacted slowly at room temperature and after a reaction time of 21 h 21% of the diallene was still present in the reaction mixture together with a 45% yield of the cycloadduct (7). The structure was assigned on the basis of spectroscopic data. At higher temperatures extensive dimerization of the diallene occurred. The dimers were actually formed slowly even at room

¹ H. Hopf and F. T. Lenich, *Chem. Ber.*, 1974, **107**, 1891.

² L. Skattebøl, *Tetrahedron*, 1967, **23**, 1107.

³ K. Kleveland and L. Skattebøl, *Acta Chem. Scand.*, 1975, **B29**, 827.

⁴ K. Kleveland and L. Skattebøl, *Acta Chem. Scand.*, 1975, **B29**, 191.

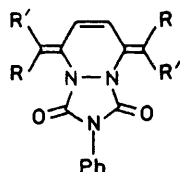
⁵ R. Kuhn and H. Fischer, *Chem. Ber.*, 1961, **94**, 3060.

⁶ M. Makosza and W. Wawrzyniewicz, *Tetrahedron Letters*, 1969, 4659; M. Makosza, *Pure Appl. Chem.*, 1975, **43**, 439.

⁷ E. V. Dehmlow and J. Schönefeld, *Annalen*, 1971, **744**, 42.

temperature and longer reaction times did not improve the yield of (7).

The situation was similar in the case of the *meso*-diallylene (4) which had only reacted partly with PTAD after 46 h at room temperature. Two main products were formed and these were separated by column chromatography on silica gel. The major component (18%) showed a mass spectrum corresponding to a 1:1 adduct with the molecular ion as the base peak. The i.r. spectrum exhibited two bands (1790 and 1735 cm^{-1}), a pattern observed also in the spectra of (6) and



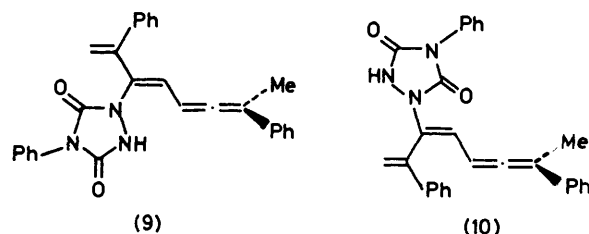
- (6) $R = R' = \text{Me}$
 (7) $R = R' = \text{Ph}$
 (8) $R = \text{Me}, R' =$

(7); these are the expected frequencies for symmetric and asymmetric in-plane carbonyl stretching vibrations of succinimides.⁸ The ^1H n.m.r. spectrum was in complete agreement with the unsymmetrical structure (8) for this adduct. Two singlets (δ 1.21 and 2.25) were assigned to the methyl groups pointing towards and away from the carbonyl group, respectively; the vinyl protons appeared as a widely separated AB quartet [δ 6.32 (d) and 8.44 (d)] where the down-field doublet is the proton deshielded by the adjacent phenyl group. It is worth noting that the vinyl protons of the adduct (7) appear as a singlet at δ 6.42 which must mean that the phenyl group in this case is twisted in such a way as to minimize the deshielding effect. The second product (15%) exhibited spectral properties quite different from those of (8), but the mass spectrum shows that it is an isomer. In the i.r. spectrum the carbonyl band appears at 1690 cm^{-1} and a weak maximum at 1950 cm^{-1} is probably due to an allenic grouping. The ^1H n.m.r. spectrum shows the presence of one methyl group, four vinyl protons, and fifteen aromatic protons. The molecular ion is the base peak in the mass spectrum, but the appearance of an ion (m/e 257) due to the loss of the triazolidinedione fragment is significant. The longest wavelength maximum in the u.v. spectrum (293 nm) suggests a triene chromophore. On the basis of these data we have assigned structure (9) or (10) to this adduct which is, formally, the product of an 'ene' reaction. The results available do not allow a distinction between these two geometrical isomers.

Reactions of either (2) or (3) with other common but less reactive dienophiles were unsuccessful. Tetracyanoethylene reacted rapidly at -30°C with (2) to give an intractable dark mixture. The result was not

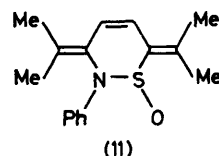
⁸ T. Woldbæk, P. Klæboe, and D. H. Christensen, *Acta Chem. Scand.*, 1976, **A30**, 531, 547; R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. (C)*, 1967, 1905.

encouraging using maleic anhydride since all attempts led to viscous polymeric material. The tetraphenyldiallylene (3) reacted only slowly at room temperature with the same dienophiles and *N*-phenylmaleimide to give complex mixtures in all cases. Considering the



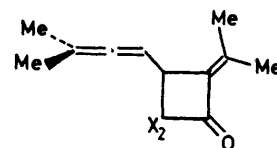
similar reactivity of (3) and (4), the latter was not treated with either of the above reagents.

Sulphonylamines behave as dienophiles in reactions with conjugated dienes.⁹ The reaction of tetramethyldiallylene (2) with sulphonylaniline gave the Diels-Alder adduct (11) in 64% yield as the only isolable product. The structural assignment was based on similar spectral



information as obtained for the other adducts. The ^1H n.m.r. spectrum was quite conclusive with singlets for each of the four non-equivalent methyl groups and a characteristic AB quartet for the vinylic protons.

An excess of (2) reacted with diphenylketene, generated *in situ*, to give two products in 76 and <4% yields, respectively. The major component was shown to be a 1:1 adduct from the mass spectrum. It was most probably a [2+2] cycloadduct since the i.r. spectrum revealed an allenic band (1965 cm^{-1}) and maxima (1730, 1660 cm^{-1}) compatible with an $\alpha\beta$ -unsaturated cyclobutanone structure.¹⁰ The latter is supported by the u.v. maxima at 224 and 245 nm. The structure (12) for



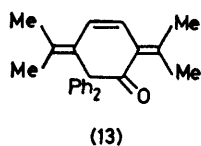
- (12) $X = \text{Ph}$
 (14) $X = \text{Cl}$

the adduct was confirmed by the ^1H n.m.r. spectrum. Besides resonances due to aromatic protons, the two non-equivalent allenyl methyl groups give rise to two doublets as a result of the coupling of each with the allenyl hydrogen; two broad singlets arise from the vinylic methyl groups while the cyclobutyl hydrogen is coupled with the allenyl hydrogen.

⁹ H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes,' Academic Press, New York-London, 1967, p. 316.

¹⁰ M. Bertrand, J.-L. Gras, and J. Gore, *Tetrahedron Letters*, 1972, 2499.

The minor product which was obtained reasonably pure was isomeric with (12) as evidenced by the mass spectrum. The loss of a C_3H_5 fragment from the molecular ion results in the base peak at m/e 287. This is also the most important fragmentation in the case of the adduct (6). The i.r. spectrum shows no allenic absorption, but a strong carbonyl band at 1695 cm^{-1} is present. Four different methyl groups were apparent from the 1H n.m.r. spectrum, and a quartet [δ 6.25 (d) and 6.59 (d)] is characteristic of vicinal non-equivalent vinyl hydrogens; the spectrum is actually quite similar to that of the sulphonylaniline adduct (11). The u.v. maximum at 295 nm is comparable to that observed for (6). All the evidence is in agreement with the Diels-Alder adduct (13). The reaction of diphenylketen with



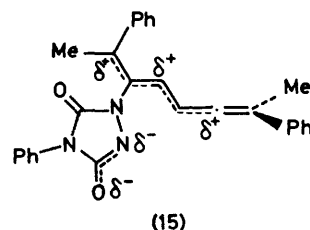
tetraphenyldiallene (3) was unsuccessful since the diallene dimerized and oligomerized under the reaction conditions. Consequently, addition to *meso*-(4) was not attempted.

Dichloroketen, generated *in situ*, reacted with an excess of (2) to give the cyclobutanone (14) in 35% yield. The assignment was based on spectral data similar to those recorded for the adduct (12). The molecular ion was not observed in the mass spectrum; the highest mass number measured corresponds to $M - Cl$, which also is the base peak.

Because of the mutual orthogonality of π bonds in cumulative systems, only the inner π bonds of the diallene (1) are conjugated, the π electrons of the outer bonds being quite localized as a first approximation. A Diels-Alder reaction will have to follow a concerted symmetry allowed [$\pi 4_s + \pi 2_s$] process or a multistep pathway. The conjugated diallenes are unique as dienes because the terminal substituents extend perpendicularly to the plane of the conjugated double bonds; consequently, a cisoid conformation required for the concerted Diels-Alder reaction will exhibit severe steric hindrance to both *exo* and *endo* approach of the dienophile. On the other hand, compared with normal conjugated dienes diradical or dipolar intermediates derived from reactions of these diallenes and dienophiles will enjoy increased stabilization as a result of electron delocalization.

The formation of the adduct (8) from *meso*-(4) and PTAD are not explained by a concerted process which demands a symmetrical structure of the product. Several examples are known where PTAD undergoes cycloadditions by stepwise processes;^{11,12} the stereo-

chemical outcome is then governed by the cyclization of the intermediate. Addition of PTAD to the central carbon of the allenic linkage gives an intermediate which is depicted as the zwitterion (15) although we cannot exclude a corresponding diradical. Subsequent ring closure of (15) yields the adduct (8). The 'ene' product (9) or (10) can also result from the same intermediate¹²



or from a concerted process. It is reasonable to assume that tetraphenyldiallene (3) also reacts by a stepwise process. It was expected that tetramethyldiallene (2) would undergo cycloadditions faster than either (3) or (4), but the drastic increase in reactivity observed suggests a change of mechanism; a concerted process would, in this case, be sterically favoured compared with (3) and (4). The formation of (11) is particularly surprising since sulphonylaniline reacts very slowly even at elevated temperatures with terminally substituted conjugated dienes.¹³ Whatever the mechanism might be, terminal substituents of conjugated diallenes strongly influence their reactivity in cycloaddition reactions. In this connection it is interesting to note that diallene itself is quite reactive towards a variety of dienophiles.¹

Allenes undergo cycloaddition reactions with ketenes to yield $\alpha\beta$ -unsaturated cyclobutanones,^{14,15} in most cases probably by a concerted symmetry allowed [$\pi 2_s + \pi 2_a$] process; hence, the formation of the adducts (12) and (13) was expected. The more nucleophilic the central carbon of the allenic linkage, the more reactive is the allene towards ketens.¹⁴ This is also consistent with our results. However, the formation of the [4 + 2] cycloadduct (13) was quite unexpected. Reactions of conjugated dienes with keten have in no case resulted in Diels-Alder products, despite careful analysis of the reaction mixtures.¹⁶ Ketens exhibit a clear preference for [2 + 2] cycloadditions, in agreement with our observations.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer for KBr discs, unless otherwise stated. 1H N.m.r. spectra were recorded with Varian A-60A and HA-100 15C spectrometers for solutions in deuteriochloroform (unless otherwise stated) with tetramethylsilane as internal standard. U.v. spectra were measured with a Cary 14 spectrophotometer. Mass spectral data were obtained using an AEI MS 902 mass spectrometer at 70 eV. Chromatographic materials included Woelm silica gel (0.063—

¹¹ R. Huisgen, W. E. Konz, and V. Schnegg, *Angew. Chem. Internat. Edn.*, 1972, **11**, 715.

¹² E. K. von Gustorf, D. V. White, B. Kim, D. Hess, and J. Leitich, *J. Org. Chem.*, 1970, **35**, 1155.

¹³ G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem.*, 1962, **74**, 135.

¹⁴ P. R. Brook, J. M. Harrison, and K. Hunt, *J.C.S. Chem. Comm.*, 1973, 733.

¹⁵ W. T. Brady, J. D. Stockton, and A. D. Patel, *J. Org. Chem.*, 1974, **39**, 236.

¹⁶ R. Huisgen and P. Otto, *Tetrahedron Letters*, 1968, 4491.

0.20 mm) for column chromatography and Woelm silica gel F for analytical t.l.c. Reactions were conducted under nitrogen atmosphere in anhydrous solvents.

Reaction of (E,E)-2,5-Diphenylhexa-2,4-diene with Dibromocarbene.—(a) *Dibromocarbene generated by phase-transfer catalysis.* A 50% aq. NaOH solution (12.00 g, 150 mmol NaOH) was added in one portion to the diene (2.343 g, 10.0 mmol), triethylbenzyl-ammonium chloride (25 mg) and 96% ethanol (0.4 ml) in bromoform (25 ml). The mixture was stirred for 1 h at 0 °C and thereafter for 45 h at room temperature. Water was added to the mixture which was then worked up in the usual way with dichloromethane. Evaporation of solvents gave a residue. Crystallization from light petroleum (b.p. 80—110 °C) gave *meso*-(E,E)-2,2,2',2'-tetrabromo-3,3'-dimethyl-3,3'-diphenylbicyclopropyl (1.171 g), m.p. 179—180 °C (lit.⁴ m.p. 180 °C). Some racemic bis-adduct (208 mg) crystallized from light petroleum (b.p. 60—80 °C) and had m.p. 167—169 °C (decomp.) [Found: C, 41.7; H, 3.5. $C_{20}H_{18}Br_4$ requires C, 41.6; H, 3.4%; ν_{max} , 695, 605, and 587 cm^{-1} (CBr); $\delta(CCl_4)$ 7.29 (10 H, s, 2 × ArH), 2.09 (2 H, s, 2 × cyclopropyl H), and 1.79 (6 H, s, Me). Column chromatography of the mother liquor gave an oil (3.137 g) which according to t.l.c. contained both the adducts and two other products. On the basis of the 1H n.m.r. spectra the total yield of bis-adducts were estimated to 3.0 g (53%) and a *meso*:racemic ratio of 55:45.

(b) *Dibromocarbene generated by potassium *t*-butoxide and bromoform.* The method was essentially as previously described⁴ except that a 5:1 ratio of bromoform to diene and twice as much pentane was used. A mixture of *meso* and racemic bis-adducts in a ratio of 73:27 was obtained in 87% yield. Pure *meso* bis-adduct was separated by crystallization from light petroleum.

2,5-Bis-(2-methylethylidene)-8-phenyl-1,6,8-triaza[4.3.0]-bicyclonon-3-ene-7,9-dione (6).—A solution of freshly sublimed PTAD (5) (1.040 g, 5.9 mmol) in dichloromethane (65 ml) was added dropwise with stirring to diallene (2) (0.800 g, 5.9 mmol) in dichloromethane (15 ml) at -78 °C. Immediate decolourisation of the red PTAD solution occurred. After addition was completed, the clear solution obtained was allowed to attain room temperature. T.l.c. showed the presence of only one substance. The product (1.601 g, 87%) crystallized from benzene-light petroleum (b.p. 60—80 °C) and had m.p. 184.0—185.5 °C (decomp.) [Found: C, 70.0; H, 6.3%; *M* (mass spec.) 309.148. $C_{18}H_{19}N_3O_2$ requires C, 69.9; H, 6.2%; *M*, 309.147. ν_{max} , 1765 and 1710 cm^{-1} (CO); λ_{max} (EtOH) 222 (ϵ 21 000) and 276 nm (18 900); δ 1.88 (6 H, s, 2 × Me), 1.96 (6 H, s, 2 × Me), 6.49 (2 H, s, 2 × vinylic H), and 7.18—7.78 (5 H, m, ArH).

2,5-Bis(diphenylmethylidene)-8-phenyl-1,6,8-triaza[4.3.0]bicyclonon-3-ene-7,9-dione (7).—A solution of freshly sublimed PTAD (5) (0.800 g, 4.5 mmol) in dichloromethane (65 ml) was added dropwise with stirring to diallene (3) (1.750 g, 4.6 mmol) suspended in dichloromethane (25 ml). After 21 h at room temperature, analytical t.l.c. indicated that the reaction was still incomplete. After removal of solvent under reduced pressure, the dark residue was chromatographed (2 × 75 cm column, chloroform as eluant). Unchanged diallene (3) (360 g, 21% of the original material) was recovered. The second component eluted was the adduct (7) (960 mg, 45%). A sample crystallized from carbon tetrachloride had m.p. 233—236 °C (decomp.). Elemental analyses were unsatisfactory [Found: *M* (mass spec.), 557.210. $C_{38}H_{27}N_3O_2$ requires *M*, 557.210.3]; ν_{max} ,

1780 and 1735 cm^{-1} (CO); λ_{max} (EtOH) 241 (ϵ 26 500) and 350 nm (25 100); δ 6.42 (2 H, s, 2 × vinylic H), 7.24 (5 H, s, ArH), 7.30 (10 H, s, 2 × ArH), and 7.32 (10 H, s, 2 × ArH).

Reaction of PTAD (5) with meso-Diallene (4).—Freshly sublimed PTAD (5) (0.700 g, 4.0 mmol) in dichloromethane (65 ml) was added as before to *meso*-diallene (4) (1.030 g, 4.0 mmol) dissolved in dichloromethane (30 ml). After 46 h at room temperature, analytical t.l.c. indicated that reaction was still incomplete. After removal of solvent under reduced pressure, the dark residue was chromatographed [2 × 80 cm column, benzene-chloroform (1:1) as eluant]. Unchanged *meso*-diallene (4) (320 mg, 31%) eluted first, followed by two products in the indicated order: 4-phenyl-1-[1-(1-phenylvinyl)hexa-1,3,4-trienyl]-1,2,4-triazolidine-3,5-dione (9) (261 mg, 15%). A sample crystallized from carbon tetrachloride had m.p. 178—180 °C (decomp.) [Found: C, 77.6; H, 5.5%; *M* (mass spec.) 433.179. $C_{28}H_{23}N_3O_2$ requires C, 77.6; H, 5.4%; 433.178.9]; ν_{max} , 1690 cm^{-1} (CO); λ_{max} (heptane) 222 (ϵ 17 800), 248 (14 500), and 293 nm (9 300); δ 2.19 (3 H, s, Me), 5.47—6.33 (5 H, m, 4 × vinylic H and 1 NH), and 7.00—7.80 (15 H, m, 3 × ArH). 8-Phenyl-*syn-anti*-2,5-bis-(1-phenylethylidene)-1,6,8-triaza[4.3.0]bicyclonon-3-ene-7,9-dione (8) (309 mg, 18%). A sample crystallized from carbon tetrachloride had m.p. 147.0—148.5 °C (decomp.). Elemental analyses were unsatisfactory [Found: *M* (mass spec.), 433.177.9. $C_{28}H_{23}N_3O_2$ requires *M*, 433.178.9]; ν_{max} , 1790 and 1735 cm^{-1} (CO); λ_{max} (cyclohexane) 217 (ϵ 18 400) and 286 nm (20 100); δ 1.21 (3 H, s, Me), 2.25 (3 H, s, Me), 6.32 (1 H, d, *J* 5.5 Hz, vinylic H), 6.43—7.37 (15 H, m, ArH), and 8.44 (1 H, d, *J* 5.5 Hz, vinylic H).

3,6-Bis-(2-methylethylidene)-2-phenyl-1,2-thiazine 1-Oxide (11).—The diallene (2) (2.405 g, 17.9 mmol) and freshly distilled sulphinyaniline (2.472 g, 17.8 mmol) were dissolved in cyclohexane (*ca.* 5 ml) and stirred at room temperature for 17 h to give a pale yellow paste. The mixture was triturated with cold ether-light petroleum (b.p. 40—65 °C) to give the product (3.09 g, 64%) as a powder. A sample crystallized from benzene-light petroleum (b.p. 40—65 °C) had m.p. 135—137 °C (decomp.) [Found: C, 70.2; H, 7.0. $C_{16}H_{19}NOS$ requires C, 70.3; H, 7.0%; ν_{max} , 3 070 (aromatic CH) and 1 595 cm^{-1} (conj. C=C); λ_{max} (EtOH) 283 (ϵ 17 300) and 316 nm (12 900); δ 1.61 (3 H, s, Me), 1.86 (3 H, s, Me), 1.97 (3 H, s, Me), 2.05 (3 H, s, Me), 6.28 (1 H, d, *J* 11.5 Hz), 6.76 (1 H, d, *J* 11.5 Hz, vinylic H), and 6.92—7.44 (5 H, m, ArH). The product decomposes slowly with time. Small amounts of water in the solvent cause formation of sulphur dioxide from sulphinyaniline; the adduct from diallene (2) and sulphur dioxide³ is then a by-product of the reaction.

Reaction of Diphenylketen with the Diallene (2).—A solution of diphenylacetyl chloride (2.19 g, 9.5 mmol) in hexane (50 ml) was added dropwise with stirring to a solution of the diallene (2) (2.00 g, 14.9 mmol) and triethylamine (1.09 g, 10.8 mmol) in hexane (40 ml) under reflux. After 20 h under reflux t.l.c. analysis revealed the presence of at least 5 components. The amine hydrochloride was filtered off, the filtrate washed with water until neutral and dried. Evaporation of solvent gave a residue which was chromatographed [2 × 80 cm column, ether-light petroleum (1:50) as eluant]. A total of 659 mg (33%) of unchanged diallene was first eluted and then two products in the following order: (i) 4-isopropylidene-3-(3-methylbuta-1,2-dienyl)-2,2-diphenylcyclobutanone (12) (2.362 g, 76%). A sample

crystallised from pentane had m.p. 51.5–53 °C [Found: C, 88.1; H, 7.5%; M (mass spec.) 328.1804. $C_{24}H_{24}O$ requires C, 87.8; H, 7.4%; M , 328.1825], λ_{\max} (cyclohexane) 224 (ϵ 16 600) and 245 nm (14 400); $\delta(CCl_4)$ 1.57 (3 H, d, J 3 Hz, Me), 1.66 (3 H, d, J 3 Hz, Me), 1.80br (3 H, s, Me), 2.14 (3 H, d, J 1.5 Hz, Me), 4.18 (1 H, m, cyclobutyl H), 4.52 (1 H, m, allenyl H), and 7.05–7.50 (10 H, m, ArH).

(ii) 5,5-Diphenyl-3,6-bis-(2-methylethylidene)-cyclohexen-4-one (13) was obtained contaminated with diphenylketen dimers in ca. 4% yield; ν_{\max} (film) 1 695 cm^{-1} (CO); λ_{\max} (cyclohexane) 248 (ϵ 11 200) and 295 nm (14 100); $\delta(CCl_4)$ 0.95 (3 H, s, Me), 1.67 (3 H, s, Me), 1.78 (3 H, s, Me), 1.91 (3 H, s, Me), 6.25 (1 H, d, J 11 Hz, vinylic H), 6.59 (1 H, d, J 11 Hz, vinylic H), and 7.0–7.5 (m, ArH).

2,2-Dichloro-4-isopropylidene-3-(3-methylbuta-1,2-dienyl)-cyclobutanone (14).—A solution of triethylamine (0.87 g, 8.6 mmol) in ether (40 ml) was added dropwise to a solution of the diallene (2) (2.0 g, 14.9 mmol) and dichloroacetyl

chloride (1.1 g, 7.4 mmol) in ether (30 ml) under reflux and with stirring. After 20 h t.l.c. analysis revealed the presence of two products. The reaction mixture was worked up as described above for (12). Chromatography [2×80 cm column, ether–light petroleum (1 : 10) as eluant] gave as the main product the adduct (14) (640 mg, 35%) as a slightly yellow liquid [Found: $M - Cl$ (mass spec.), 209.0745. $C_{12}H_{14}ClO$ requires $M - Cl$, 209.0733]; ν_{\max} 1 965 (C=C=C), 1 765 (CO), and 1 655 cm^{-1} (C=C); λ_{\max} (cyclohexane) 249 nm (ϵ 12 100); $\delta(CCl_4)$ 1.71 (6 H, t, J 2.5 Hz, Me), 1.87 (3 H, d, J 2 Hz, Me), 2.19 (3 H, d, J 2.5 Hz, Me), 3.86 (1 H, m, cyclobutyl H), and 5.05 (1 H, m, allenyl H).

The minor product was not obtained pure enough for structural elucidation.

[8/399 Received, 6th March, 1978]