

Rearrangements in the Cycloaddition of Tetracyanoethylene to 3-Methylenecyclohexa-1,4-dienes and Homofulvenes

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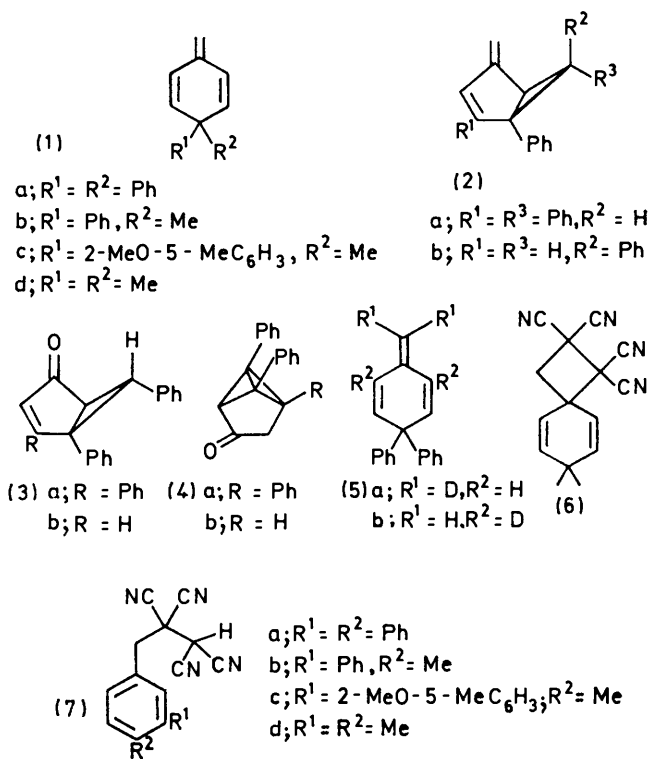
Reaction of tetracyanoethylene with 6,6-disubstituted derivatives of 3-methylenecyclohexa-1,4-diene gives rise to four classes of adduct: spiro[3,5]nona-5,8-dienes, bicyclo[4,3,0]nona-1,4-dienes, bicyclo[4,3,0]nona-1,3-dienes, and tetracyanopropylbenzene derivatives. The relative proportions of these depend both on the detailed structure of the triene and on the solvent. Both these results and the stereochemistry of the bicyclic adducts are discussed in terms of an ionic mechanism in which the lifetime of the initially formed zwitterion is important. The structures of products from tetracyanoethylene and 2-methylenebicyclo[3,1,0]hex-3-ene derivatives are also consistent with an ionic addition mechanism.

THE addition of dienophiles to conjugated olefins proceeds, when possible, by the thermally allowed Diels-Alder reaction ($\pi 2_s + \pi 4_s$)¹ or, occasionally, by the Alder 'ene' reaction² ($\pi 2_s + \pi 2_s + \sigma 2_s$), both of which involve a six-membered cyclic transition state. In cases where steric constraints hinder or prevent the attainment of such a transition state other cycloadditions permitted by orbital symmetry conservation are sometimes observed³ but, more commonly, powerful dienophiles react by a nonconcerted process which appears to involve ionic intermediates. Examples of this latter class are well established with tetracyanoethylene (TCNE)⁴ and in its reaction with substituted styrenes⁵ the variation in rate with both solvent and substituent (ρ ca. -7) is consistent with a polar mechanism.

There have been relatively few studies on the reaction of TCNE with other conjugated polyenes where the molecular geometry is unfavourable to a concerted cycloaddition.⁶ We wished to examine systems where the initial carbonium ion might undergo rearrangement prior to collapse of the intramolecular ion pair. Accordingly we chose the reaction of TCNE with some 6,6-disubstituted derivatives of 3-methylenecyclohexa-1,4-diene (1) and some derivatives of 4-methylenebicyclo[3,1,0]hex-2-ene (2), a choice based on the following considerations: (i) in neither case is the simple Diels-Alder reaction possible nor is the geometry of (2) favourable for an Alder ene reaction; (ii) the exocyclic methylene group should be the favoured site for electrophilic attack on both steric and electronic grounds, which limits the number of possible products; (iii) the cation resulting from this initial attack should be readily formed, being at least as stable as an allylic cation; (iv) there exists a considerable number of studies on the rearrangements of analogous cations.⁷⁻⁹

The methylenecyclohexadienes (1a-d) were pre-

pared by Wittig reactions on the corresponding ketones,¹⁰⁻¹³ but no satisfactory general route to appro-



priately substituted homofulvenes (2) was found. Compound (2a) was obtained from a Wittig reaction on the corresponding bicyclo[3,1,0]hex-3-en-2-one (3a), available from basic cleavage of (4a),¹⁴ but the analogous base

⁷ K. von Auwers and K. Ziegler, *Annalen*, 1921, **425**, 217; K. M. Baker, K. H. Bell, and B. R. Davis, *Austral. J. Chem.*, 1968, **21**, 294.

⁸ A. J. Waring, *Adv. Alicyclic Chem.*, 1967, **1**, 208.

⁹ H. Hart, T. R. Rogers, and J. Griffiths, *J. Amer. Chem. Soc.*, 1969, **91**, 754; R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, 1968, **90**, 7144, 7146.

¹⁰ H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 1962, **84**, 4527.

¹¹ H. E. Zimmerman and G. Jones, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 2753.

¹² V. Arkley, F. M. Dean, A. Robertson, and P. Sidisunthorn, *J. Chem. Soc.*, 1956, 2322.

¹³ E. D. Bergmann and R. Corrett, *J. Org. Chem.*, 1956, **21**, 107; 1958, **23**, 1507.

¹⁴ A. S. Monahan, *J. Org. Chem.*, 1968, **33**, 1441.

¹ A. Wasserman, 'Diels-Alder Reactions,' Elsevier, New York, 1965.

² A. M. Lautzenheiser and P. W. LeQuesne, *Tetrahedron Letters*, 1966, 2293.

³ A. T. Blomquist and J. C. Meinwald, *J. Amer. Chem. Soc.*, 1959, **81**, 667; W. Schäfer and H. Hellmann, *Angew. Chem. Internat. Edn.*, 1967, **6**, 518.

⁴ J. K. Williams, *J. Amer. Chem. Soc.*, 1959, **81**, 4013; D. S. Matteson, J. J. Drysdale, and W. H. Sharkey, *ibid.*, 1960, **82**, 2855.

⁵ J. K. Williams, D. W. Wiley, and B. C. McKusik, *J. Amer. Chem. Soc.*, 1962, **84**, 2210.

⁶ C. A. Stewart, *J. Amer. Chem. Soc.*, 1962, **84**, 117; J. J. Eisch and C. R. Husk, *J. Org. Chem.*, 1966, **31**, 589.

cleavage of (4b)¹⁵ to (3b) failed. The *endo*-analogue (2b) was obtained from photolysis of (1a).¹⁶ To assist in structural elucidation of some of the products it was necessary to prepare certain ²H-labelled derivatives (5a and b). Introduction of the deuteriated exocyclic methylene group by the Wittig reaction¹⁷ was straightforward and the analogue of (1a) with ²H-labelling in both positions α to the methylene group was prepared from [2,2,6,6-²H₄]-4,4-diphenylcyclohexanone. Basic cleavage of (4a) in deuterium oxide gave negligible incorporation at position 1 or 3 in the product (although, naturally, there was complete incorporation at position 6). However, [1-²H]-(3a) was obtained by cyclisation¹⁴ of [1-²H]-1-diazo-3-(1,2,3-triphenylcycloprop-2-enyl)propan-2-one to the ²H-analogue of (4a) followed by basic cleavage.

Reactions of compounds (1a—d) in solution with 1 equiv. of TCNE gave four general types of adduct, together in some cases with small amounts of unidentified products. The dimethyl-substituted triene (1d) gave rise only to the spirononadiene (6) and the aromatic adduct (7d), and we found that the former rearranged to the latter in polar solvents. From (1a) the adduct types (7)—(9) were obtained, the proportions depending on the solvent (see later) and their structures were assigned on the basis of elemental analysis and spectra (¹H n.m.r. and u.v.). In addition, the adduct (7a) was degraded to 3,4-diphenylbenzoic acid by alkaline permanganate. Confirmation of these structures and in particular the stereochemistry of (8a) and (9a) rests on the various coupling

In the case of the non-conjugated adduct (8a) the two large allylic coupling constants $J_{1,3}$ and $J_{2,4}$ argue for

TABLE 1

		N.m.r. data for adducts (8a) and (9a) in [² H ₆]acetone (<i>J</i> in Hz)					
		τ	$J_{1,n}$	$J_{2,n}$	$J_{3,n}$	$J_{4,n}$	$J_{5,n}$
(8a) *	H-1	3.70					
	H-2	4.64	<0.5				
	H-3	5.12	1.9	2.4			
	H-4	5.63	3.1	2.5	9.8		
	H-5	6.09	<0.5	<i>a</i>	3.1	<i>a</i>	
	H-6	6.40	<0.5	<i>a</i>	2.1	<i>a</i>	17.5
(9a) *	H-1	3.21					
	H-2	3.50	6.1				
	H-3	5.15	<0.5	<0.5			
	H-4	5.54	<0.5	3.5	10.3		
	H-5	5.95	<0.5	<i>a</i>	<0.5	<i>a</i>	
	H-6	6.60	<0.5	<i>a</i>	<0.5	<i>a</i>	18.8

* For atom numbering see illustrated formulae.

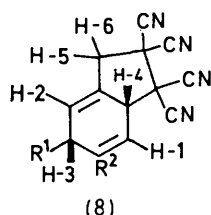
* These coupling constants could only be estimated as sums or differences.

TABLE 2

		N.m.r. data for adducts (8b and c), (9c), and (10) *						$J_{3,4}$ / Hz	$J_{5,6}$ / Hz
		τ (CDCl ₃)							
		H-1	H-2	H-3	H-4	H-5	H-6		
(8b)		4.12 ^a	4.22 ^a	6.08	6.12	6.40	6.64	10.0	17.0
(8c)		4.20	4.20	5.36	6.12	6.44	6.66	10.0	17.0
(9c)		3.82	3.82	5.62	6.13	6.52	6.84	9.8	17.5
(10)		3.83 ^a	4.14 ^a	5.98	5.98	6.34	6.60		16.0

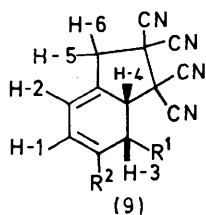
* For atom numbering see illustrated formulae.

* In these cases the assignments of H₁ and H₂ could, conceivably be interchanged (as could also those for H₅ and H₆ in 8b) but that presented is considered more probable in view of likely chemical shifts relative to (8a).



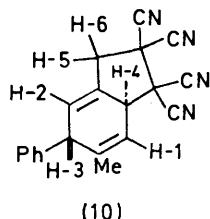
(8)

- a; R¹ = R² = Ph
 b; R¹ = Ph, R² = Me
 c; R¹ = 2-MeO-5-MeC₆H₃,
 R² = Me

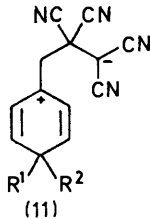


(9)

- a; R¹ = R² = Ph
 b; R¹ = Ph, R² = Me
 c; R¹ = 2-MeO-5-MeC₆H₃,
 R² = Me



(10)



(11)

constants, obtained (as were the chemical shift assignments) with the aid of appropriately deuteriated derivatives (Tables 1 and 2).

¹⁵ S. Masamune, *Tetrahedron Letters*, 1965, 945; W. M. Jones and R. S. Pyron, *ibid.*, p. 479.

¹⁶ H. E. Zimmerman, P. Hackett, D. F. Ivers, and B. Schröde, *J. Amer. Chem. Soc.*, 1967, **89**, 5971; 1971, **93**, 3653.

H-3 and H-4 being pseudoaxial. Moreover, $J_{3,4}$ is more consistent with a *cis* (diaxial) rather than a *trans* (axial-equatorial) coupling.¹⁸ Finally, the small size of the vicinal coupling constants $J_{1,4}$ and $J_{2,3}$ indicates a dihedral angle close to 90°. For adduct (9a) however the allylic coupling constants $J_{1,3}$ and $J_{2,4}$ are markedly different, suggesting that whereas H-4 is pseudoaxial H-3 is pseudoequatorial. It is unfortunate that there exist no suitable comparative data for vicinal couplings in cyclohexa-1,3-dienes since the uncertainties in the conformational parameters of these very rigid systems is likely to render Karplus-type predictions unreliable. At first it seemed to us surprising that a cisoid diene system should be isolated from the reaction of (1a) with TCNE but a further Diels-Alder reaction is unlikely owing to great strain in the resulting product.

Adducts of the types (7)—(9) with aryl migration occurring exclusively were also obtained from the methyl aryl compounds (1b and c) although, owing to difficulties in separation and the instability of some of the components, notably (7b and c), not all proved isolable. Their structures were readily deduced by comparison of

¹⁷ S. E. Cremer and R. J. Chorrat, *Tetrahedron Letters*, 1966, 419.

¹⁸ E. W. Garbisch and M. G. Griffith, *J. Amer. Chem. Soc.*, 1968, **90**, 3590; D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2335.

their spectra with those of the corresponding diphenyl compounds. Among the minor components (<10% total products) there was found, especially from reactions conducted in the more polar solvents such as acetonitrile, the *trans*-isomer (10), although we were unsuccessful in separating it completely from the *cis*-isomer (8b).

The relative proportions of the various adduct types varied with both the structure of the starting triene and the solvent (Table 3). Rates of reaction, too, were very

TABLE 3

Effect of solvent variation on adduct composition (%)

Solvent	From (1a)			From (1c)		
	(7a)	(8a)	(9a)	(7c)	(8c)	(9c)
Benzene	0	50	50	12	24	64
Chloroform	2	52	46	20	18	62
Dimethoxyethane	12	58	30	62	20	18
Acetonitrile	48	40	12	70	18	12

Estimated from n.m.r. data and reproducible to $\pm 2\%$ except in acetonitrile where the reproducibility was $\pm 4\%$.

sensitive to polarity of solvent and for compound (1a) were roughly estimated to be of the order $10^4 : 10 : 1$ in acetonitrile, dimethoxyethane, and benzene, respectively. From competition experiments the relative reactivities were found to be (1d) > (1c) > (1a) although here the overall difference in reactivity was only of the order of a factor of 6. Taken together these observations suggest that the rate-determining step involves the formation of an ionic intermediate and that this is the unrearranged zwitterion (11).

On this basis several aspects of the cycloaddition merit comment. Firstly the preference (exclusive in the case of the diphenyl compounds) for the formation of *cis*-isomers implies considerable stereoelectronic control. No argument invoking concerted migration and capture with orbital symmetry conservation¹⁹ can account for this since the transition state for (8), being vinylogous to that leading to (9), would require capture on the opposite side. We suggest instead that collapse of the rearranged zwitterion (12) is fast compared to conformational movement of the side chain (Figure), analogous to that observed by Kramer²⁰ in the reaction of TCNE with anetholes, but in the present case the closure to give a five-membered ring, being much faster than that giving a four-membered ring,²¹ results in less sensitivity to solvent polarity. Further migration of the phenyl group *cis* to the side chain appears to be favoured in comparison with *trans*—possibly as a result of electrostatic interaction between the migrating group and anionic centre.

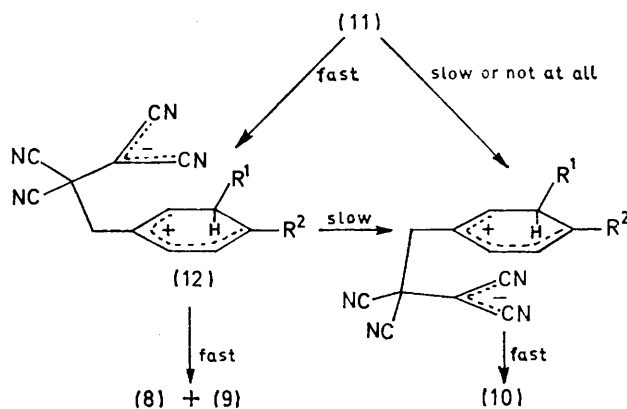
Next, in the case of the trienes (1b and c) only products of aryl migration were observed; * this is consistent with the greater migratory aptitude of aryl groups relative to methyl.²² Moreover the strong (but here not exclusive) preference for *cis*-adduct formation implies that aryl

* It is possible that small amounts of adducts of type (7) from methyl migration were produced but could not be isolated for characterisation owing to their labile nature.

¹⁹ R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Gmbh, Weinheim-Bergstr., 1970.

migration *trans* to the side chain may be comparable in rate with interconversion of the two side chain conformers (12), on the assumption that these are formed with similar facility.

The proportion of aromatised adducts (7) relative to bicyclo- (or spiro-) nonadienes increases with polarity of solvent and is greatly assisted by traces of hydroxylic solvents. These will not only stabilise, and hence increase the lifetime, of the zwitterion (11) but may also assist directly in the necessary proton transfers. The



FIGURE

absence of significant quantities of (7) from reactions conducted in benzene indicates that intramolecular proton transfer in (11) is unimportant.

While the relative proportions of the non-conjugated (8) to conjugated (9) adducts does not vary dramatically with solvent there is nevertheless a consistent increase in the proportion of the former (Table 3) as the polarity of the solvent increases; thus probably reflects steric effects on the collapse of the ion (11). Molecular models suggest that the transition state for the latter is more crowded and this energy differential will increase the closer the transition states resemble the products.

Only with the triene (1d) did we observe the formation of the spiro-adduct (6), and in no solvent did reaction lead to detectable quantities of the bicyclononadiene adducts (8) and (9) although traces may have been formed. This again is consistent with the lower migratory aptitude of methyl relative to the aryl group. In polar solvents, particularly hydroxylic ones, ring opening of (6) to (7) occurred although it was slower than the direct reaction of TCNE with (1d) leading to (7) in these solvents. [Reaction in pyridine led by elimination of HCN to (13).] Since the aryl-substituted trienes also gave rise to considerable quantities of aromatised adducts (7) under these conditions it is probable that the difference in behaviour of (1d) is merely one of degree.

Reaction of TCNE with the homofulvene (2a) gave

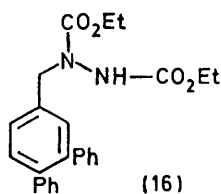
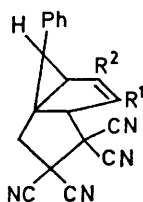
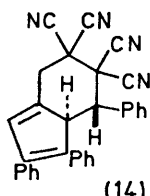
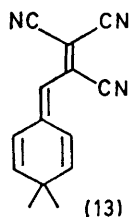
²⁰ B. D. Kramer, Thesis, Harvard University, 1968.

²¹ E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 198.

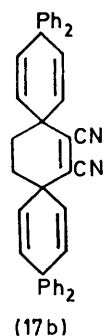
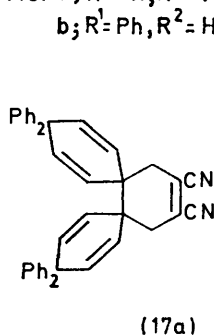
²² J. D. Roberts and C. M. Regan, *J. Amer. Chem. Soc.*, 1953, **75**, 2069; J. D. Roberts and M. Halman, *ibid.*, 5759.

an adduct whose structure was established as (14), analogous to that claimed in the reaction of dienophiles with 1,2,3,5,6-pentamethyl-4-methylenebicyclo[3,1,0]hex-2-ene.²³ This could arise by a two-step ionic process or, as has been proposed, by a concerted [$\sigma 2_a + \pi 4_s + \pi 2_s$] process. However the major adduct formed from homo-fulvene (2b) is clearly different in type and the n.m.r. data were consistent with either (15a) or (15b). A mechanism involving 'slither',^{9,24} of the three membered ring in the

that this arose from another adduct. However there was no evidence that compounds analogous to (8)—(10) were produced even as intermediates. Dicyanoacetylene gave large amounts of deep-coloured polymeric products together with a small amount of 2:1 adduct whose n.m.r. data were consistent only with structure (17a) or, less probably, (17b). The mode of formation of this unexpected product must at present be a matter for speculation.



(15) a; R¹ = H, R² = Ph
b; R¹ = Ph, R² = H



zwitterion prior to collapse can readily account for such products and, since the rearranged zwitterion leading to (15a) is stabilised further by conjugation to the phenyl group, we prefer it to (15b).

We also examined the reaction of the triene (1a) with azodicarboxylic ester and dicyanoacetylene and in both cases observed different behaviour from that found with TCNE. The former reacted slowly in an apparently second-order reaction which, adjudged by the disappearance of (1a), proceeded at the same rate in both acetonitrile and carbon tetrachloride. From the product mixture we were able to isolate and characterise only the adduct (16) and there was evidence (from n.m.r. studies)

EXPERIMENTAL

Solvents were purified and dried according to reported procedures. Chromatographic separations were carried out on Mallinckrodt Silicar CC7. ¹H N.m.r. spectra were obtained with a Varian HA100 (100 MHz) spectrometer (tetramethylsilane as internal standard). U.v. spectra were recorded for solutions in 95% ethanol, unless otherwise stated, with a Cary 14M-40 spectrophotometer. 4,4-Di-substituted cyclohexa-2,5-dienones were prepared by literature methods. The 6,6-disubstituted derivatives (1a—d) of 3-methylenecyclohexa-1,4-diene were prepared by Wittig reactions on the appropriate ketones. Compounds (1a) and (1d) were purified by recrystallisation and distillation respectively and were identical with reported samples.^{16,25} Compounds (1b) and (1c), after purification by chromatography under nitrogen, were obtained as oils which polymerised very rapidly in air; n.m.r. data indicated that they contained <2% impurities.

3-Methyl-6-methylene-3-phenylcyclohexa-1,4-diene (1b) (yield 70%) had τ (CCl₄) 2.7—3.1 (5H, m), 3.92 (2H, d, *J* 10 Hz), 4.36 (2H, d, *J* 10 Hz), 5.2 (2H, s), and 8.60 (3H, s).

3-(2-Methoxy-5-methylphenyl)-3-methyl-6-methylene-cyclohexa-1,4-diene (1c) (yield 80%) had τ (CCl₄) 2.9—3.4 (3H, m), 3.87 and 3.91 (4H, q, *J*_{AB} 10 Hz), 5.24 (2H, s), 6.24 (3H, s), 7.76 (3H, s), and 8.44 (3H, s).

[²H₂]Methyltriphenylphosphonium Bromide.—To a solution from sodium (0.1 g) in deuterium oxide (30 ml) was added methyltriphenylphosphonium bromide (10 g); the mixture was kept at room temperature for 2 h, neutralised (conc. HBr) and, evaporated to dryness. The residue was extracted with ethanol. On addition of ether the product (9.3 g) crystallised and was dried *in vacuo* (P₂O₅). N.m.r. data indicated an isotopic purity of 95%.

4,4-Diphenyl[2,6-²H₂]cyclohexa-2,5-dienone.—To a solution of 4,4-diphenylcyclohexanone (10 g)²⁶ in dioxan (50 ml) were added deuterium oxide (4.0 ml) and potassium carbonate (0.25 g), and the mixture was refluxed under nitrogen for 24 h. After removal of the solvent *in vacuo* the residue was taken up in dioxan with fresh deuterium oxide and refluxed for a further 24 h. After repetition of this procedure the residue was extracted with dry chloroform; n.m.r. examination of the crystalline product showed that α -deuteration was essentially complete (>95%). To this product (3.0 g) in dry tetrahydrofuran (30 ml) was added dropwise with stirring during 30 min a solution of NNN-trimethylanilinium perbromide²⁷ (11.5 g; 86% available bromine by titration) in dry tetrahydrofuran. After filtration the solution was diluted with deuterium oxide (10 ml) and extracted with dry dichloromethane (5 × 20 ml).

²³ H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, 1968, **90**, 5612; T. M. Brennan and R. K. Hill, *ibid.*, 5614.

²⁴ R. Askani, *Angew. Chem. Internat. Edn.*, 1970, **9**, 167.

²⁵ K. von Auwers and K. Muller, *Ber.*, 1911, **44**, 1602.

²⁶ F. G. Bordwell and K. M. Wellmann, *J. Org. Chem.*, 1963, **28**, 2544.

²⁷ A. Marquet and J. Jacques, *Bull. Soc. chim. France*, 1962, 90.

To the extract containing the crude dibromo-ketone were added in turn lithium carbonate (10 g), dry dimethylformamide (50 ml), deuterium oxide (3 ml), and anhydrous lithium bromide (6.0 g). The mixture was gradually warmed, the dichloromethane and tetrahydrofuran being slowly distilled off through a Vigreux column, after which more deuterium oxide (3 ml) was added and the mixture was heated under reflux for 4 h. The cooled mixture was filtered, dichloromethane (200 ml) was added to the filtrate, and the organic layer was then washed with water (3 × 200 ml), dilute hydrochloric acid (3 × 100 ml), and saturated sodium hydrogen carbonate solution (2 × 50 ml), dried (MgSO₄), and evaporated. The residue was chromatographed to give the product (0.56 g). N.m.r. data indicated an isotopic purity of ca. 85%.

4-Methylene-1,6-endo-diphenylbicyclo[3,1,0]hex-2-ene (2b).—A solution of 6-methylene-3,3-diphenylcyclohexa-1,4-diene in *t*-butyl alcohol (270 ml) and methanol (50 ml) was irradiated under nitrogen with a 125 W medium-pressure mercury lamp through a Vycor filter for 2.5 h. After removal of the solvent the products were separated by chromatography (eluant 10% dichloromethane-hexane). There were obtained starting material (125 mg), the crude product (115 mg), and secondary photoproducts (150 mg) identified as a mixture of the *exo*- and *endo*-isomers of 1,5-diphenylspiro[2,4]hepta-4,6-diene.^{16,28} The crude primary photoproduct fractions from four such irradiations were combined and crystallised from light petroleum to give the pure product, m.p. 57—58.5° (lit.,¹⁶ 59°).

4-Methylene-1,2,6-exo-triphenylbicyclo[3,1,0]hex-2-ene (2a).—To a suspension of methyltriphenylphosphonium bromide (1.2 g) in dry benzene (20 ml) under nitrogen was added butyl-lithium (1.3 ml of 2.15M-solution in pentane). After stirring for 2 h a solution of 4,5,6-*exo*-triphenylbicyclo[3,1,0]hex-3-en-2-one (0.75 g)¹⁴ in benzene (40 ml) was added. The mixture was refluxed for 2 h then filtered; the filtrate was evaporated to dryness and the residue was taken up in hot methanol. On cooling, the product (0.68 g) crystallised and after being dried *in vacuo* (P₂O₅) had m.p. 123—124° (Found: C, 93.5; H, 6.6. C₂₅H₂₀ requires C, 93.7; H, 6.3%), λ_{max.} (CH₂Cl₂) 240, 251, and 298 nm (ε 18,700, 20,500, and 15,200), τ (CCl₄) 2.7—3.3 (15H, m), 3.88 (1H, s), 4.91br (1H, s), 4.96br (1H, s), 7.15br (1H, d, *J* 4 Hz), and 7.50 (1H, d, *J* 4 Hz).

Deuteration of 1-Diazo-3-(1,2,3-triphenylcycloprop-2-enyl)propan-2-one.—A solution of the diazo-ketone (3.0 g) in dioxan (10 ml) was added with vigorous stirring to deuterium oxide (10 ml) in which sodium (0.1 g) had dissolved. After 5 min the oil which had separated crystallised and was immediately filtered off and dried *in vacuo*. Crystallisation from light petroleum at -30° gave the product (1.85 g), in which incorporation of deuterium at the 1-position was >95%.

7,7,8,8-Tetracyano-3,4-diphenyl-cis-3H,6H-bicyclo[4,3,0]nona-1,4-diene (8a).—A solution of compound (1a) (0.50 g) and TCNE were heated under reflux in dry benzene until the initial deep red colour had faded to a pale yellow (4 h). The solvent was taken off *in vacuo* and the residue dissolved in the minimum of hot chloroform. The crystals which separated on cooling crystallised from chloroform-ether to give the product (0.26 g) m.p. 173—174° (Found: C, 80.3; H, 4.8; N, 15.1. C₂₅H₁₆N₄ requires C, 80.6; H, 4.3; N, 15.1%), λ_{max.} 248 nm (ε 8700). The deuterated derivatives were prepared in the same manner.

7,7,8,8-Tetracyano-4,5-diphenyl-cis-5H,6H-bicyclo[4,3,0]-

nona-1,3-diene (9a).—The mother liquors from the foregoing chloroform solution were evaporated to dryness and the residue was taken up by warming in ether-carbon tetrachloride (1:1). The crystals which separated on cooling crystallised from chloroform-ether to give the product (0.23 g), m.p. 211—214° (Found: C, 80.5; H, 4.4; N, 15.4. C₂₅H₁₆N₄ requires C, 80.6; H, 4.3; N, 15.1%), λ_{max.} 318 nm (ε 14,100).

1,2-Diphenyl-4-(2,2,3,3-tetracyanopropyl)benzene (7a).—To a solution of compound (1a) (100 mg) in acetonitrile (2 ml containing 1% of water) was added TCNE (50 mg); the solution was kept at room temperature for 30 min, then evaporated. Recrystallisation from carbon tetrachloride gave the product (0.12 g), m.p. 155—156° (decomp.) (Found: C, 80.4; H, 4.3; N, 14.9. C₂₅H₁₆N₄ requires C, 80.6; H, 4.3; N, 15.1%), λ_{max.} (CH₂Cl₂) 241, 257, and 263 nm (ε 24,500, 11,200, and 10,100), τ [(CD₃)₂CO] 2.3—2.9 (13H, m), 3.97 (1H, s), and 6.1 (2H, s). Oxidation with alkaline permanganate gave *o*-terphenyl-4'-carboxylic acid.²⁹

1,1,2,2-Tetracyano-7,7-dimethylspiro[3,5]nona-5,8-diene (6).—Compound (1d) (0.357 g) and TCNE (0.384 g) were kept in dry acetonitrile (2 ml) for 2 min. Evaporation of solvent and recrystallisation from ether gave the product (0.43 g), m.p. 86.5—87° (Found: C, 7.2; H, 4.9; N, 22.7. C₁₁H₁₂N₄ requires C, 72.6; H, 4.8; N, 22.6%), τ (CDCl₃) 3.9 (4H, ABq, *J* 10 Hz), 6.9 (2H, s), 8.86 (3H, s), and 8.9 (3H, s).

1,2-Dimethyl-4-(2,2,3,3-tetracyanopropyl)benzene (7d).—A solution of compound (1d) (60 mg) in acetonitrile (1 ml) and acetic acid (1 ml) was treated with TCNE (64 mg) in acetonitrile (1 ml). The reaction appeared to be complete after 1 s, and removal of the solvent *in vacuo* at room temperature followed by recrystallisation of the residue twice from ether gave the product (40 mg), m.p. 131—133° (decomp.) (Found: C, 72.3; H, 5.0; N, 22.7. C₁₅H₁₂N₄ requires C, 72.6; H, 4.9; N, 22.6%), τ (CDCl₃) 2.84 (3H, s), 5.91 (1H, s), 6.53 (2H, s), and 7.74 (6H, s).

3,3-Dimethyl-6-(2,3,3-tricyanoprop-2-enylidene)cyclohexa-1,4-diene (13).—A solution of compound (6) (100 mg) in acetonitrile (1 ml) and pyridine (1 ml) was kept at room temperature for 4 h, after which time all the starting material had reacted. From the complex mixture of products there was isolated (by preparative t.l.c. on silica gel GF₂₅₄ followed by recrystallisation from carbon tetrachloride) the orange crystalline product (20 mg), m.p. 151—153° (Found: C, 75.8; H, 5.2; N, 19.1. C₁₄H₁₁N₃ requires C, 76.0; H, 5.0; N, 19.0%), λ_{max.} (EtOH) 244, 308, 324, and 433 nm (ε 4100, 3600, 3470, and 38,800), τ (CDCl₃) 2.35 (1H, d, *J* 10 Hz), 3.35 (1H, d, *J* 10 Hz), 3.44 (1H, d, *J* 10 Hz), 3.63 (1H, d, *J* 10 Hz; 1H, s), and 8.72 (6H, s).

Reaction of Compound (1b) with TCNE.—Compound (1b) (255 mg) and TCNE (160 mg) in benzene (1 ml) for 3 days gave 7,7,8,8-Tetracyano-4-methyl-3-phenyl-cis-3H,6H-bicyclo[4,3,0]nona-1,4-diene (8b) (103 mg), m.p. 163—165° (from ether) (Found: C, 77.3; H, 4.5; N, 17.9. C₂₀H₁₄N₄ requires C, 77.4; H, 4.5; N, 18.1%), λ_{max.} (EtOH) 263 and 270 nm (ε 510 and 340). Concentration of the mother liquors gave crystals (10 mg) which appeared to consist of 30% of (8b) together with 70% of the *trans*-isomer (10) (Found: C, 77.3; H, 4.7; N, 17.7%), λ_{max.} 263 and 270 nm (ε 550 and 320). In addition to the resonances from (8b) the n.m.r. spectrum showed τ (CDCl₃) 3.83 (1H, m), 4.14 (1H,

²⁸ N. K. Hamer and M. E. Stubbs, *Chem. Comm.*, 1970, 1013.

²⁹ K. Alder, H. Decker, and R. Leinan, *Annalen*, 1950, 570, 214.

m), 5.98 (2H, m), 6.34, 6.60 (2H, ABq, J 16 Hz), and 8.20 (3H, s) attributable to (10).

Reaction of Compound (1c) with TCNE.—Similarly compound (1c) (0.65 g) and TCNE (0.36 g) gave, after recrystallisation first from ether then from chloroform-ether, 7,7,8,8-tetracyano-3-(2-methoxy-5-methylphenyl)-4-methyl-cis-3H,6H-bicyclo[4,3,0]nona-1,4-diene (8c) (52 mg), m.p. 190—192°, λ_{\max} (EtOH) 280 and 288 nm (ϵ 3400 and 3270) (Found: C, 74.8; H, 5.3; N, 15.7. $C_{22}H_{18}N_4O$ requires C, 74.6; H, 5.1; N, 15.8%).

The mother liquor from the first crystallisation, on cooling to -30° followed by recrystallisation of the solid deposited from ether-carbon tetrachloride, gave 7,7,8,8-tetracyano-5-(2-methoxy-5-methylphenyl)-4-methyl-cis-5H,6H-bicyclo[4,3,0]nona-1,3-diene (9c) (240 mg), m.p. 163—165°, λ_{\max} (EtOH) 286 nm (ϵ 9230) (Found: C, 74.2; H, 5.4; N, 15.3. $C_{22}H_{16}O$ requires C, 74.6; H, 5.1; N, 15.8%).

Product Studies.—The proportions of the various adduct types from reactions in different solvents (all carefully dried) were estimated from n.m.r. data for the mixture (peak heights); calibration was performed with mixtures of known composition. In the case of adducts from compound (1c) it was assumed that the heights of the methoxy-signals (not being coupled to any other protons) would be insensitive to structural changes.

Relative rates for reactions of compound (1a) with TCNE in various solvents were qualitatively estimated from the rate of disappearance of the deep colour of the charge-transfer complex. Relative reactivities of the various trienes in $[^2H_6]$ benzene were followed by the addition of small portions of TCNE to a solution of a mixture of (1a) and the other triene and observing the relative rates of disappearance of the terminal methylene protons by n.m.r.

3,3,4,4-Tetracyano-2,8,9-triphenylbicyclo[4,3,0]nona-6,8-diene.¹⁴—A solution of compound (2a) (160 mg) and TCNE (60 mg) in benzene (2 ml) was stored until the initial deep red colour had faded to a pale yellow. Removal of the solvent and recrystallisation of the residue from ether gave the product (106 mg), m.p. 155—157° [resolidified and remelted at 207—208° (decomp.)] (Found: C, 83.0; H, 4.4; N, 12.2. $C_{31}H_{20}N_4$ requires C, 83.0; H, 4.5; N, 12.5%), λ_{\max} 239 and 305 nm (ϵ 27,900 and 6400), τ ($CDCl_3$) 2.2—3.5 (15H, complex m), 5.88 (1H, d, J 12.3 Hz, absent when the $[5-^3H]$ -derivative of the diene was used), 6.39 (2H, s,

separated into an ABq on addition of $[^2H_6]$ benzene, J 14 Hz), and 6.96 (1H, d, J 12.3 Hz). The same product was obtained from reaction in acetonitrile and in both cases n.m.r. data for the crude reaction mixture showed it to be the main component.

Reaction of TCNE with Methylene-1,6-endo-diphenylbicyclo[3,1,0]hex-2-ene.—Compound (2b) (213 mg) and TCNE (107 mg) were dissolved in dry acetonitrile (1 ml) and the solution was kept at room temperature for 1 h. The solvent was removed and the residue was chromatographed on silica; the major product was eluted with dichloromethane. Recrystallisation from chloroform-ether gave the adduct (15a or b) (63 mg), m.p. 212—214° (Found: C, 79.8; H, 4.4; N, 15.6%; M^+ , 372. Calc. for $C_{25}H_{16}N_4$: C, 80.6; H, 4.3; N, 15.1%; M^+ , 372), λ_{\max} 267 nm (ϵ 12,800).

The same product was isolated, but in smaller yield when the reaction was carried out with benzene as solvent (24 h at room temperature).

Diethyl 1-(3,4-Diphenylbenzyl)hydrazine-1,2-dicarboxylate (16).—The reaction of ethyl azodicarboxylate (90 mg) and compound (1a) (120 mg) in acetonitrile for 14 days in the dark gave, after evaporation of the solvent and recrystallisation from carbon tetrachloride-ether, the product (125 mg), m.p. 173—175° (Found: C, 71.5; H, 6.2; N, 6.4. $C_{25}H_{26}N_2O_4$ requires C, 71.8; H, 6.2; N, 6.7%), τ ($CDCl_3$) 2.60 (3H, s), 2.80 (10H, s), 3.35br (1H, s), 4.20 (2H, s), 5.71 and 5.77 (4H, two q, each J 7 Hz), and 8.67 and 8.74 (6H, two t, each J 7 Hz).

Reaction of Compound (1a) with Dicyanoacetylene.—To a solution of dicyanoacetylene (100 mg) in benzene (1 ml) under nitrogen was added compound (1a) (244 mg). After 6 h the solution was chromatographed on silica (carbon tetrachloride then dichloromethane as eluant). The latter eluate gave a crystalline adduct (17a or b) (60 mg), m.p. 282—283° (decomp.) (from carbon tetrachloride) (Found: C, 87.2; H, 5.7; N, 4.9%; M^+ , 564. Calc. for 1 : 2 adduct: C, 89.4; H, 5.7; N, 5.0%; M^+ , 564), τ ($CDCl_3$) 2.60—3.10 (20H, m), 3.92 (4H, d, J 10 Hz), 4.44 (4H, d, J 10 Hz), and 7.50 (4H, s).

When the reaction was repeated with a smaller ratio of dicyanoacetylene to (1a) the yield of product was increased but under all conditions the major product was a red polymer and considerable amounts of (1a) remained unchanged.

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