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# Cycloadditions of the 2-Methylallyl Cation to Conjugated Dienes

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The 2-methylallyl cation has been generated in liquid sulphur dioxide from 2-methylallyl iodide and silver trichloroacetate in the presence of cyclopentadiene, cyclohexadiene, and furan. Some new bridged seven-membered ring olefins, 3-methylbicyclo[3,2,1]octa-2,6-diene, 3-methylenebicyclo[3,2,1]oct-6-ene, and 3-methylbicyclo-[3,2,2]nona-2,6-diene, have been isolated, and it is suggested that they arise from a concerted cycloaddition of the allylic cation to the conjugated diene.

EVANS pointed out <sup>1</sup> that the electrons in the transition state of a Diels-Alder addition simulate the behaviour (of electrons) in a benzene structure. Consequently, since the discovery of the tropylium ion by Doering and Knox <sup>2</sup> one could have been tempted to test theory by searching for cycloadditions whose transition state is electronically related to the tropylium ion, *i.e.*, the cycloaddition of a conjugated diene to an allylic cation to form the cyclohept-4-enyl cation (Scheme). That such



a concerted process is symmetry-allowed has been pointed out by Hoffmann and Woodward.<sup>3</sup> We now record the first clear examples for this class of cycloaddition.<sup>4</sup>

It seemed unlikely that we could work in highly acidic media such as sulphuric acid and fluorosulphuric acid, or in liquid sulphur dioxide, if an excess of antimony pentafluoride was present. In these conditions a number of acyclic and cyclic allylic carbonium ions had been observed and studied largely to establish their spectral properties.<sup>5</sup> Even in liquid sulphur dioxide at  $-60^{\circ}$  the allylic cations tended markedly to dimerise and polymerise.<sup>5a</sup>

## RESULTS

The cycloadditions required conditions in which a conjugated diene could survive to react with the allylic cation. After attempts to prepare stable allyloxonium <sup>6a</sup> and allyl nitrilium salts 60 by Meerwein's methods had failed, we decided to generate the 2-methylallyl cation in situ, i.e., in the presence of the conjugated diene under as mild conditions as possible. Since antimony pentachloride could not be used as electrophilic catalyst without damage to the diene, we tried silver salts. Initial experiments with 2-methylallyl iodide and silver tetrafluoroborate in liquid sulphur dioxide followed by quenching of the mixture in methanol were not successful. A key observation was that the nature of the silver counter-ion profoundly affected the reaction. While silver acetate and silver benzoate gave the corresponding 2-methylallyl esters nearly quantitatively, the nucleophilicity of trichloroacetate ion from silver trichloroacetate was sufficiently suppressed. In liquid sulphur dioxide (and some dichloromethane as a cosolvent) 2-methylallyl iodide reacted smoothly with silver trichloroacetate and cyclopentadiene (a 1.5 molar excess of the diene being used). Quenching of the mixture with aqueous ammonia yielded 3-methylbicyclo[3,2,1]octa-2,6-diene (I), 3-methylenebicyclo[3,2,1]oct-6-ene (II), and a less stable, unidentified compound [with a g.l.c. retention time only slightly greater

M. G. Evans, Trans. Faraday Soc., 1939, 35, 824; see also
 M. G. Evans and E. Warhurst, *ibid.*, 1938, 34, 614.
 W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc.,

<sup>&</sup>lt;sup>2</sup> W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 1954, **76**, 3203.

<sup>&</sup>lt;sup>3</sup> R. Hoffmann and R. B. Woodward, J. Amer. Chem. Soc., 1965, 87, 2046.

<sup>&</sup>lt;sup>4</sup> This work was briefly described (by H. M. R. H.) at the University of Pisa on June 23rd, 1967, and is covered by British Patent Application No. 11,342/67 (March 10th, 1967).

<sup>&</sup>lt;sup>5</sup> (a) G. A. Olah and M. B. Comisarow, J. Amer. Chem. Soc., 1964, 86, 5682; (b) G. A. Olah and C. U. Pittman, jun., Adv. Phys. Org. Chem., 1966, 4, 305; (c) N. C. Deno, Progr. Phys. Org. Chem., 1964, 2, 161.

<sup>Org. Chem., 1964, 2, 161.
(a) H. Meerwein, 'Methoden der Organischen Chemie,'</sup> Houben-Weyl, vol. 6/3, Thieme, Stuttgart, 1965, p. 325; (b) J. Goerdeler, *ibid.*, vol. 11/2, 1958, p. 618.

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than that of (I)] which we consider to be most likely (IVa). Remarkably, 2-methylallyl trichloroacetate was formed in a minor amount (ca. 2%). Under the same reaction conditions (except for a 2 molar excess of diene) cyclohexadiene gave 30% of 2-methylallyl trichloroacetate. After quenching, 3-methylbicyclo[3,2,2]nona-2,6-diene (III) was isolated in 20% yield. An experiment with furan in benzene solvent vielded 2-(2'-methylallyl)furan (IVb). The structures of all four compounds were determined by mass and n.m.r. spectroscopy.

# DISCUSSION

It is interesting that the 2-methylallyl cation can survive in the presence of trichloroacetate ion to react with conjugated dienes. Very likely, the allylic cation does will have to show whether trichloroacetate ion approaches the carbonium ion preferentially from the exo direction. The postulated tertiary trichloroacetic esters (VIa and b) appear to be unstable, even in solution at  $0^{\circ}$ . Thus, before the reaction mixture had been quenched with ammonia, some decomposition to olefins and polymers had usually occurred.

The observed olefin ratio (I)/(II) = 7:3 from (VIa) indicates Saytzeff control and corresponds to what one would expect from a reactive tertiary alkyl substrate.<sup>9</sup> In the case of the cyclohexadiene derivative we have so far detected the Saytzeff olefin (III) only. An equilibration of products before or during the quenching procedure cannot certainly be ruled out.

By which mechanism is the furan derivative (IVb)



not exist as such but rather as an ion-pair <sup>7</sup> stabilised by the bidentate interaction with the carboxylate counterion. We believe that the tertiary carbonium ion (Va, b) is formed next before collapsing to covalent trichloroacetate (VIa and b) and to bicyclic olefins. Pre-



sumably (Va and b), is a 'harder' carbonium ion than the 2-methylallyl cation,8 and is therefore intercepted readily by the hard trichloroacetate ion, which functions as a built-in quenching reagent towards (Va and b). In any case, the conjugated diene competes effectively with trichloroacetate for the intermediate 2-methylallyl cation. The stereochemistry of attack by trichloroacetate on (Va and b) is not known, and further studies

While a straightforward electrophilic subformed? stitution might appear as the most direct route, it must be considered that (IVb) can also arise from the tricyclic carbonium ion (Vc) by fragmentation.<sup>10</sup> Reversibility of Diels-Alder additions with furans is well established,<sup>11</sup> and in this case the driving force for fragmentation would be provided by formation of a relatively stable alkoxyallyl carbonium ion followed by regeneration of the aromatic furan sextet.\*

# EXPERIMENTAL

Materials.--Silver trichloroacetate 12 was made by rapid mixing of equimolar amounts of silver nitrate and sodium trichloroacetate in saturated aqueous solution, the precipitate being washed successively with water, acetone, and ether, and dried in vacuo. Titration of silver ion gave a figure within 3% of theoretical. Silver trichloroacetate was stored at  $-\,80^\circ$  in the dark, since it decomposes at room temperature and on prolonged exposure to light.

2-Methylallyl iodide <sup>13</sup> was prepared from 2-methylallyl chloride and a slight excess of sodium iodide in saturated acetone solution. After 3 hr. at room temperature the mixture was washed with water, dried, and distilled rapidly from mercury at reduced pressure (b. p. 28°/3-5 mm.). 2-Methylallyl iodide (40% yield) was pure by gas chromatographic and spectroscopic standards and stored at  $-80^{\circ}$ .

<sup>9</sup> G. M. Fraser and H. M. R. Hoffmann, Chem. Comm., 1967,

561. <sup>10</sup> C. A. Grob and P. W. Schiess, Angew. Chem. Internat. Edn.,

<sup>16</sup> C. A. Grob and P. W. Schless, Angew. Chem. Internat. Lan., 1967, 6, 5, 6.
<sup>11</sup> F. A. L. Anet, *Tetrahedron Letters*, 1962, 1219, and references therein; see also P. Bosshard and C. H. Eugster, Adv. Heterocyclic Chem., 1966, 7, 377.
<sup>12</sup> See H. M. R. Hoffmann, J. Chem. Soc., 1965, 6748 for the analogous preparation of silver toluene p-sulphonate.
<sup>13</sup> C. A. McDowell, F. P. Lossing, I. H. S. Henderson, and J. B. Farmer, Canad. J. Chem., 1956, 34, 345.

<sup>\*</sup> Note added in proof: After this paper had been submitted we became aware of a publication by R. C. Cookson, M. J. Nye, and G. Subrahmanyam, J. Chem. Soc. (C), 1967, 473, who isolated a bicyclic adduct from the reaction of furan with an intermediate generated from di-( $\alpha$ -bromobenzyl) ketone and sodium iodide in acetonitrile. This adduct was shown to rearrange to the 2-substituted furan derivative on treatment with base or acid.

<sup>&</sup>lt;sup>7</sup> S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc. Special Publ. No.* 19, 1965, p. 109; see also H. M. R. Hoffmann, *Ann. Reports*, 1966, **62**, 322.

<sup>&</sup>lt;sup>8</sup> R. G. Pearson and J. Songstad, J. Amer. Chem. Soc., 1967, 89. 1827.

2-Methylallvl trichloroacetate. To a cooled  $(-30^{\circ})$  mixture of 2-methylallyl alcohol (1.66 ml.) and trichloroacetyl chloride (2.24 ml.), 2,6-lutidine (2.42 ml.) was added dropwise with stirring. The temperature was allowed to rise slowly to room temperature, and the mixture shaken with water, twice with dilute hydrochloric acid, and water. The product was dried over molecular sieves and distilled at 70°/8-10 mm. (Found: C, 33.3; H, 3.4; Cl, 48.8. Calc. for  $C_6H_7Cl_3O_2$ : C, 33·2; H, 3·2; Cl, 48·9%);  $n_D^{25} =$ 1.4650. N.m.r. at 60 Mc./sec. in carbon tetrachloride: \* 8.12 (3H) singlet; 5.12 (2H) singlet; 4.73 (2H) olefinic doublet, which shows further splittings on expansion.

Cycloaddition Products.--Compounds (I), (II), and (III) were markedly volatile and isolated by preparative g.l.c. on a 20 ft. dicyanoethyl ether column. This volatility always caused some loss during work-up and the given yields should therefore not be regarded optimum.

3-Methylbicyclo[3,2,1]octa-2,6-diene (I) and 3-Methylenebicyclo[3,2,1]oct-6-ene (II).-Methylallyl iodide (2.7 ml.; 0.025 mole) in dichloromethane (5 ml.) was stirred into a suspension of silver trichloroacetate (6.8 g.; 0.025 mole) in cyclopentadiene (3.1 ml.; 0.038 mole) in liquid sulphur dioxide (ca. 100 ml.) at  $-50^{\circ}$  during 5 min. The mixture was stirred at  $-50^{\circ}$  for 90 min., and allowed to warm to room temperature with evaporation of sulphur dioxide. After addition of dichloromethane (30 ml.) the mixture was filtered, and the filtrate concentrated at reduced pressure to ca. 15 ml. (the n.m.r. spectrum of this solution indicated that about 2% of 2-methylallyl trichloroacetate had been formed). The mother-liquor was added slowly to stirred concentrated aqueous ammonia cooled in ice, and the organic layer washed with water, dried, and further concentrated. Preparative g.l.c. yielded 3-methylbicyclo[3,2,1]octa-2,6-diene (I) [40%; retention time (r.t.) relative to benzene 1.6], 3-methylenebicyclo [3,2,1] oct-6-ene (II) (16%; r.t. relative to benzene 1.95), and a third, less stable, unidentified product (IVa?) (16%; r.t. 1.7).

Structural proof for (I) and (II). Mass spectroscopy showed the two compounds to be isomeric and to have the molecular formula  $C_9H_{12}$  (Found: 120.0936. Calc. for  $C_9H_{12}$ : 120.0939). The n.m.r. spectrum of (I) is similar to that of bicyclo[3,2,1]octa-2,6-diene; <sup>14</sup> 8.45 (3H), sharp signal, expands to quintet [methyl protons on C(9)]; 7.7-8.4 (4H) complex; 7.35 (2H) broad multiplet [H(1), H(5)]; 4.3 (2H) quartet; 3.8 (1H) quartet. Double irradiation of H(1) and H(5) reduces the two quartets at 3.8 and 4.3 to an AB type quartet ( $J_{6,7} = 5.6$  c./sec.); superposed on the peak at 4.25 are further transitions due to H(2). Double irradiation at the centre of H(2) changes the intensities of the C(9) quintet without producing a clean triplet.

N.m.r. spectrum of (II). 7.6-8.7 (6H) complex; 7.47 (2H) broad multiplet [H(1), H(5)]; 5.43 (2H) triplet [methylene protons on C(9)],  $J_{2,9} = J_{4,9} = 2.1$  c./sec.; 4.21 (2H) ill-resolved quintet [H(6), H(7)]. Decoupling the bridgehead protons reduces the olefinic quintet to a doublet  $(I_{(6,7),83} = 0.6 \text{ c./sec.}; \text{ see reference } 15a \text{ for a similar ex-}$ ample of long-range coupling in norbornenes). Double irradiation of H(8a) collapses the olefinic quintet to a triplet;  $|J_{1,7} + J_{6,7}| = 2.4$  c./sec. (see reference 15).

3-Methylbicyclo[3,2,2]nona-1,6-diene (III).—Methylallyl iodide (2.7 ml.) in dichloromethane (5 ml.) was stirred into a suspension of silver trichloroacetate (6.8 g.) in cyclohexadiene (4.7 ml.) and liquid sulphur dioxide (ca. 100 ml.) at  $-50^{\circ}$  during 5 min. The mixture was stirred for 90 min. at  $-50^{\circ}$  and worked up as described for (I) and (II). The n.m.r. spectrum of the mother-liquor indicated the formation of ca. 30% of 2-methylallyl trichloroacetate; 3-methylbicyclo[3,2,2]nona-2,6-diene (III) was isolated in 20% yield [g.l.c. retention time relative to benzene 2.7 (4.1 relative to dichloromethane] (Found: M, 134.1096. Calc. for C<sub>10</sub>H<sub>14</sub>: M, 134·1095). N.m.r. spectrum: 8·44 (3H) sharp signal, expands to quintet [methyl protons on C(10)]; 7.7-8.4 (6H) complex; 7.5 (2H) broad signal [H(1), H(5)]; 4.35 (1H) centre of a doublet of quartets which show further splittings [H(2)]; 3.98 (1H) centre of a triplet (spacings ca. 8 c./sec.), which shows further splittings; 3.63 (1H) centre of a triplet (spacings ca. 8 c./sec.) with some unresolved fine structure,  $J_{6,7} = 8.6$ ,  $J_{1,2} = 8.2$ ,  $J_{2,4} = 1.5$  c./sec. from decoupling experiments.

2-(2'-Methylallyl) furan (IV).-2-Methylallyl iodide (2.7 ml.) in benzene (5 ml.) was stirred into an ice-cooled suspension of silver trichloroacetate (6.8 g.) in furan (3.6 ml.) and benzene (25 ml.) during 30 min. After a further 10 min. the mixture was filtered and added slowly to a well-stirred solution of ammonia in dichloromethane (100 ml. solution, 0.5M) at  $-80^{\circ}$ . The mixture was allowed to reach room temperature, concentrated. and centrifuged. Preparative g.l.c. yielded (ca. 30%) of 2-(2'-methylallyl)furan (IV) as the only discernible hydrocarbon product (retention time relative to benzene 2.5) (Found: C, 77.8; H, 8.2. C<sub>8</sub>H<sub>10</sub>O requires C, 78·1; H, 8·1%); n.m.r. spectrum: 8·34 (3H) sharp signal, expands to quintet (methyl protons); 6.73 (2H) singlet (aliphatic methylene protons); 5.24 (2H) doublet which shows further splittings on expansion. The H(3), H(4), and H(5) protons show the expected <sup>16</sup> AMX pattern with  $J_{3,4} = 3.2$ ,  $J_{3,5} = 1.0$ , and  $J_{4,5} = 1.9$  c./sec.; H(3) appears as a doublet of quartets due to further splitting by the aliphatic methylene protons.

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86, 1166; (b) R. J. Abraham and H. J. Bernstein, Canad. J. Chem., 1961, 39, 216.
<sup>16</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Per-

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All other spectra were obtained in deuteriochloroform at 100 Mc./sec.; chemical shifts are given on the  $\tau$  scale with internal chloroform as standard (2.75 $\tau$ ); absolute values of J are quoted.

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