# Cycloadditions of Simple Allyl Cations to Conjugated Dienes. Optimization and Scope of the Reaction

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The cycloaddition of simple allyl cations to conjugated dienes, exemplified by the reaction of the 2-methylallyl cation to cyclohexa-1,3-diene, has been studied in detail as a function of silver counterion, solvent, and temperature. The optimum conditions involved stirring an excess of the conjugated diene with 2-methylallyl iodide and silver trifluoroacetate in isopentane at  $-78^{\circ}$  for *ca*. 6 h. 3-Methylbicyclo[3,2,2]nona-2,6-diene (2) was isolated in 30% yield. For the first time  $[4 + 3 \rightarrow 7]$  cycloadditions with open chain dienes are described; butadiene gives rise to 1-methylcyclohepta-1,4-diene (3a) (6%). Tentative indications for the formation of cycloadducts from the reactions of the 2-methylallyl cation with isoprene and 2,3-dimethylbutadiene are given. The parent allyl cation has been trapped by cyclopentadiene to give bicyclo[3,2,1]octa-2,6-diene (8). The combination of silver trifluoroacetate and isopentane is shown to be of general utility for generating carbonium ions on a preparative scale from alkyl and vinyl halides. The special problems of adding a reactive species such as an allyl cation without terminal substituents to conjugated dienes, particularly open chain derivatives, are discussed and an interesting parallel between Diels-Alder additions of benzyne at *ca*. 30° and  $[4 + 3 \rightarrow 7]$  cycloadditions of the 2-methylallyl cation has come to light.

We have shown previously that the 2-methylallyl cation can be generated from the corresponding iodide and silver trichloroacetate in the temperature range  $-50^{\circ}$  to  $10^{\circ}$  and can be intercepted by conjugated dienes to give seven-membered adducts.<sup>1</sup> The experimental conditions are crucial for the success of this reaction, and therefore a detailed study of the effect of silver counterion, solvent, and reaction temperature was in order. We have examined the cycloaddition of the 2-methylallyl cation to cyclohexa-1,3-diene under a variety of conditions (Table 1). The problems of generating, stabilizing, and trapping carbonium ions on a preparative scale have been investigated and the experience gained has been applied to a number of new cycloadditions.



SCHEME Stages of the cycloaddition of an allyl cation to a conjugated diene

In previous studies of the title reaction,  $I_{a,b}$  three consecutive stages have emerged: (i) generation of

\* That stage (i) is indeed a discrete step which precedes stage (ii) follows from the fact that the rate of precipitation of silver iodide from allylic iodide and silver salt stays the same whether cyclopentadiene is present or not.

allylic cation,\* (ii) cycloaddition proper, and (iii) stabilization of the cyclohept-4-envl cation formed (Scheme). Given this Scheme, the most important factor in optimizing the yield is the nature of the silver counterion. It had become clear earlier that a silver salt such as AgBF<sub>4</sub>, the anion of which is non-nucleophilic, is highly effective in stage (i), but can provide little if any stabilization of the intermediate carbonium ion in stage (ii), and is actually disastrous in step (iii) in that liberation of  $HBF_4$  leads to polymerization of reactants and products alike. On the other hand, electrophilic catalysts, e.g. silver benzoate and silver acetate, give only allylic esters, even in the presence of a reactive diene such as cyclopentadiene.<sup>1a</sup> Thus, the counterion, while being weakly nucleophilic and so extending the lifetime of the intermediate allylic cation, must nevertheless in stage (iii) combine with a proton to form an acid (which must not be too powerful) or with a carbonium ion to form an ester. These criteria are met by silver trichloroacetate,<sup>1a</sup> and it seemed to us that other salts, especially the trifluoroacetate could be at least equally effective. Silver trifluoroacetate is a crystalline solid, which is soluble in ether and water, and relative to the trichloroacetate it is thermally and photochemically stable and also a powerful electrophilic catalyst, especially under heterogeneous conditions.

### DISCUSSION AND RESULTS

Our initial fear that the trifluoroacetic acid liberated in step (iii) of the Scheme might destroy the reactants or the bicyclic adduct, was laid to rest when it was found that added scavengers of acid such as 2,3-dimethylbut-2-ene and 2-methoxypropene, while combining with trifluoroacetic acid during the reaction, did not affect the yield of cycloadduct in any way (Table 1, no. 3). More specifically, in those reactions where no trap

<sup>&</sup>lt;sup>1</sup> (a) H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, J. Chem. Soc. (B), 1968, 57; (b) H. M. R. Hoffmann and D. R. Joy, *ibid.*, p. 1182; (c) H. M. R. Hoffmann and N. F. Janes, J. Chem. Soc. (C), 1969, 1456.

was added the bulk of the acid was probably removed in situ by addition to cyclohexa-1,3-diene (a three molar excess of olefin being used) to give cyclohexenyl trifluoroacetate (cf. Experimental section) or it may simply be present as the cyclic dimer. As an alternative approach to the problem of liberated acid, silver 3,5-dinitrobenzoate was tried in place of trifluoroacetate, the acid produced now being insoluble in liquid sulphur dioxide (no. 4).

Of the various solvents listed in Table 1 only diethyl ether (no. 5) allows a completely homogeneous reaction. In this solvent precipitation of silver iodide proceeds readily and 2-methylallyl trifluoroacetate is formed in high yield (70%; cf. only ca. 20% under the usual heterogeneous conditions). Interestingly, when silver trifluoroacetate is used on a Diatomite support, i.e. in a highly dispersed form (no. 10), nearly the same composition of products is formed as by reaction in

### TABLE 1

Experimental conditions and yields of cycloaddition of the 2-methylallyl cation to cyclohexa-1,3-diene

				Adduct
No.	Solvent	Silver salt	T/°C	(%)
1	SO,	AgO,C·CCl,	-50	20 ª
<b>2</b>	SO,	AgO,C·CF,	-78	20
3	$SO_2$	$\operatorname{AgO}_{2}C \cdot CF_{3} + \operatorname{Acid}_{trap} b$	78	20
4	SO <sub>2</sub>	$\begin{array}{c} \operatorname{AgO}_2 C \cdot C_6 H_3 (\operatorname{NO}_2)_2 - \\ 3.5 \end{array}$	-78	15
5	Ether	AgO,C·CF,	-78	۵ 15
6	Toluene	AgO, C·CF,	-78	16 ª
7	m-Xylene-	AgO,C·CF,	-78	12 .
	isopentane $(1:1)$	<b>.</b>		
8	Benzene	AgO,C·CCl,	+5	Trace <sup>f</sup>
9	Benzene-	AgO.C.CF.	78	20 "
	isopentane $(3:1)$			
10	Isopentane	$AgO_2C \cdot CF_3$ on Diatomite	78	20 °
11	No solvent	AgO.C.CF.	0	30
12	Isopentane	AğO,C·CF,	0	25
13	Isopentane	AgO,C·CF,	-78	30

« Ref. 1a; ca. 30% 2-methylallyl trichloroacetate formed. <sup>b</sup> Scavengers of acid in the order of increasing efficiency: 2methylbut-2-ene, 2,3-dimethylbut-2-ene, and 2-methoxy-propene.  $^{\circ}$  70% 2-Methylallyl trifluoroacetate formed.  $^{\circ}$  o-(2-Methylallyl)toluene (26%) and p-(2-methylallyl)toluene (25%) are formed; in the absence of conjugated diene, these two compounds arise in 48 and 34% yield, respectively. At-tempts to precipitate AgI from 2-methylallyl iodide and Ag<sub>2</sub>CO<sub>3</sub> dispersed on molecular sieves 3A, and from the silver cation form of an ion-exchange resin (Amberlite IR-120) were and 15% yield. <sup> $\sigma$ </sup> Two (2-methylallyl)xylenes formed in 45 and 15% yield. <sup>f</sup> Other products are allylic ester and (2-methylallyl)benzene (D. R. Joy, Ph.D. Thesis, University of London, 1968). <sup> $\sigma$ </sup> (2-Methylallyl)benzene formed (16%, increased in the absence of diene to 60%).

ether, even though the reaction mixture is now heterogeneous. The common feature of the two experiments is that trifluoroacetate ion is readily available, so that just two products are formed in a relatively 'clean' reaction and little, if any, trifluoroacetic acid is liberated. In order to throw further light on the contrasting

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amounts of 2-methylallyl trifluoroacetate formed. the silver salt and 2-methylallyl iodide were allowed to react in isopentane and in ether in the absence of diene. The yields of trifluoroacetic ester were 50 and 90%, respectively; in the former case acid was also generated and some darkening of the solution occurred. Since 2-methylallyl trifluoroacetate was found to be relatively stable to trifluoroacetic acid under these conditions, the formation of the ester must somehow have been arrested in the system AgO<sub>2</sub>C·CF<sub>3</sub>isopentane. A possible side reaction is the combination of 2-methylallyl cation with 2-methylallyl iodide to give acid and polymer, formation of which is also indicated by the presence of broad peaks in the n.m.r. spectrum of the mixture. Both Deno<sup>2a</sup> and Olah<sup>2b</sup> have found that ally cations are unstable compared with alkyl cations, and that they readily undergo cyclization and polymerization. Generally, heterogeneous conditions would seem to be advantageous for the cycloaddition (cf. Table 1, no. 11), and the combination of silver trifluoroacetate in isopentane (no. 13) has been found to be optimum. Provided that the surface of the silver salt is kept free from silver iodide by efficient stirring, the precipitation of the silver salt is ca. 90% complete after 6 h.

Our results indicate that in the course of the cycloaddition in isopentane a propoportion of the diene is adsorbed on the surface of the silver salt on stirring. In the case of butadiene a stable complex with silver trifluoroacetate has been isolated (cf. Experimental section and ref. 3). On addition of 2-methylallyl iodide, the carbon-iodine bond is weakened until silver iodide is formed and the allylic cation so generated is attracted to the positive hole in the crystal lattice created by the loss of silver ion. Presumably, at this stage the carbonium ion has a longer lifetime and is more strongly 'solvated' than would be possible in solution, as the interaction with the surface of the crystal is probably far stronger than that with polar solvents. During the lifetime of the carbonium ion, cycloaddition can occur if a diene molecule is encountered, either borne by the solvent or adsorbed to an adjacent site. In the final stage, three major isolable products are released from the surface into solution, the cycloadduct, 2-methylallyl trifluoroacetate, and trifluoroacetic acid (and perhaps also some bicyclic trifluoroacetate cf. the Scheme).

Having established the optimum conditions for adding simple allyl cations to conjugated dienes, we began to investigate new and less favourable reactions. To our knowledge only cyclic dienes have so far been reported 1,4 to undergo  $[4 + 3 \rightarrow 7]$  cycloadditions \* and it was of interest to learn whether cycloadditions with simple

<sup>\*</sup> For this nomenclature, see R. Huisgen, Angew. Chem. Internat. Edn., 1968, 7, 321.

<sup>&</sup>lt;sup>2</sup> (a) N. C. Deno, Progr. Phys. Org. Chem., 1964, 2, 129 and references cited therein; (b) G. A. Olah and C. U. Pittman, jun., Adv. Phys. Org. Chem., 1966, 4, 305.

<sup>&</sup>lt;sup>3</sup> Cf. J. W. Kraus and E. W. Stern, J. Amer. Chem. Soc., 1962, 84, 2893; H. W. Quinn, Canad. J. Chem., 1967, 45, 1329. <sup>4</sup> N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, J. Amer. Chem. Soc., 1969, 91, 2283; R. C. Cookson, M. J. Nye, and G. Subrahmanyam, J. Chem. Soc. (C), 1967, 473; 1965, 2009; A. W. Fort, J. Amer. Chem. Soc., 1969, 94, 2620, 2665, 4009; A. W. Fort, J. Amer. Chem. Soc., 1962, 84, 2620, 2625, 4979.

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open-chain dienes, such as butadiene, 2,3-dimethylbutadiene, and isoprene, were feasible. From the reaction of butadiene we expected to obtain the endocyclic isomer (3a) rather than 5-methylenecycloheptene (3b), since exocyclic products had not been found in the cycloaddition to cyclohexadiene, but had in the reaction with cyclopentadiene <sup>1a</sup> because the second double bond can be introduced into the methylene-bridged seven-membered ring only at the expense of some extra strain (cf. Table 2). G.l.c. of the products from butadiene showed a single new peak (6% yield;  $R_t$ 0.35 with respect to t-butylbenzene). Unfortunately, attempts to identify the product by preparative g.l.c. and even combined g.l.c.-mass spectroscopy were not successful. However, 1-methylcyclohepta-1,4-diene (3a) could be identified conclusively by g.l.c. comparison with an authentic specimen, which was obtained from cyclohept-4-enemethanol,<sup>5</sup> by converting into the tosylate,<sup>5</sup> eliminating to 5-methylenecycloheptene (3b),56 and treating with catalytic amounts of acid.

In the case of isoprene two new products (A) (1.8%);  $R_t$  0.27 relative to t-butylbenzene) and (B) (2.9%;  $R_t$  0.33) were formed. On hydrogenation of the reaction mixture, compounds (A) and (B) decreased and a new peak appeared which had the  $R_t$  reported for authentic cis- and/or trans-1,4-dimethylcycloheptane (cf. Experimental section). Hence, it is likely that compounds (A) and (B) are the expected 1,4(or 1,5)-dimethylcyclohepta-1,4-dienes (4a) and (4b), though which is which is not known. Finally, from the reaction of 2,3-dimethylbutadiene and 2-methylallyl cation a new peak (4%) appeared which had a retention time ( $R_t$ 0.54) not inconsistent with the formation of 1,2,4-trimethylcyclohepta-1,4-diene (5). Any firm identification of compounds (4a), (4b), and (5) would require an independent synthesis.

While yields can only serve as a guide to reactivity which should be measured more precisely by competition experiments, a comparison of our results with those on the relative reactivity of dienes towards maleic anhydride (Table 2, column 5) is instructive. Open-chain dienes behave differently towards 2-methylallyl cation and maleic anhydride. For instance, while cyclohexadiene and butadiene are of comparable reactivity towards maleic anhydride, the yields with the 2-methylallyl cation amount to 30 and 6%, respectively (Table 2). Furthermore, 2,3-dimethylbutadiene reacts about five times faster than butadiene towards maleic anhydride, whereas the yield of the diene (5), whether it is formed or not, must be lower than that of compound (3a).

The energy level of the cisoid conformer of butadiene (which is required for a concerted cycloaddition) lies at least 2 kcal mol<sup>-1</sup> above that of the transoid form.<sup>6</sup> In other words, at any given moment the proportion of butadiene molecules available for cycloaddition amounts to *ca.* 4% at ambient temperature, but at





Reactions 1—5 carried out with 3 mol. equiv. of diene in isopentane at -78°; reaction 6 carried out with 2 mol. equiv. of furan in SO<sub>2</sub> at -50°.<sup>1a</sup> Reaction 7 carried out in benzene with silver trichloroacetate; 2-methylallyl trichloroacetate (60%) formed as well (D. R. Joy, Ph.D. Thesis, University of London, 1968); adducts (1a), (1b), (2), and (6) have been described previously. <sup>b</sup> Benzyne generated from o-bromofluorobenzene and magnesium at ca. room temperature except in No. 7; cf. R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967. <sup>o</sup> J. Sauer, Angew. Chem. Internat. Edn., 1967, 6, 16. <sup>d</sup> From equimolar cyclopentadiene; G. Wittig and E. Knauss, Chem. Ber., 1958, 91, 895.
<sup>o</sup> 2 Mol. equiv. of diene used; H. E. Simmons, J. Amer. Chem. Soc., 1961, 83, 1657. <sup>f</sup> G. Wittig and H. Dürr, Annalen, 1964, 672, 55. <sup>o</sup> 10 Mol. equiv. of diene. <sup>b</sup> Ca. 5 mol. equiv. of diene. <sup>c</sup> Ca. 4 mol. equiv. of diene. <sup>f</sup> Neat furan used; G. Wittig and L. Pohmer, Angew. Chem., 1955, 67, 348. <sup>k</sup> Benzyne generated from benzenediazonium-2-carboxylate in benzene; cf. R. G. Miller and M. Stiles, J. Amer. Chem. Soc., 1963, 85, 1798; L. Friedman, personal communication cited in footnote b. <sup>d</sup> F. A. L. Anet, Tetrahedron Letters, 1962, 1219.

 $-78^{\circ}$  to less than 0.7%. For 2,3-dimethylbutadiene the population of cisoid conformer will be even smaller, since the methyl groups are eclipsed in the cisoid species.

<sup>6</sup> See E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965, p. 22.

<sup>&</sup>lt;sup>5</sup> (a) See H. L. Goering and G. N. Fickes, J. Amer. Chem. Soc., 1968, 90, 2848; G. Stork and H. Landesman, *ibid.*, 1956, 78, 5129; (b) R. W. Thies, personal communication.

In Diels-Alder additions with maleic anhydride (Table 2, column 5) the dienophile is a stable molecule (at the reaction temperature and can exist unchanged in solution until it encounters a cisoid conformer, which is in fast pre-equilibrium with its transoid rotamer. In contrast, the allylic cation is at best a short-lived intermediate and, with only a one-hundredth chance that a suitable cisoid partner is available in its neighbourhood, will rapidly undergo other reactions.

Our results illustrate a general problem that arises in cycloadditions of reactive intermediates, the situation being reminiscent of [4 + 2] cycloadditions of benzyne. This compound resembles an allyl cation in the sense that it is short-lived at the temperature at which its reactions with dienes have been studied, so that the similarity in yields for both types of cycloaddition is probably no coincidence.\* Whether the formally electrophilic substitution products (6) and (7) arise from a  $[4+3 \rightarrow 7]$  cycloaddition followed by a fragmentation, has been discussed in the case of furan,<sup>1c</sup> but requires further investigation for both reactions.

Finally, we have been able to add allyl cation itself to cyclopentadiene, and have obtained bicyclo[3,2,1]octa-2,6-diene. This very reaction was mentioned as symmetry-allowed in 1965.7



Conclusions.-As in the cycloadditions of other reactive intermediates such as benzynes and carbenes, several factors determine the course of the reaction. As far as the allyl cation is concerned, it should be generated as a ' cold ' species, *i.e.* at as low a temperature as possible, and its stationary concentration throughout the reaction should remain small. Our experimental conditions are the mildest we have been able to establish so far. It seems clear that the parent allyl cation is too short-lived even under our optimum conditions and collapses preferentially to allyl trifluoroacetate. Therefore, our efforts are now directed towards developing efficient routes to more stable and yet sufficiently reactive allyl cations, especially terminally alkylated species.

With open-chain dienes, two further and more serious problems arise in that (i) the cisoid conformer is very sparsely populated at  $-78^{\circ}$  and (ii) butadiene, if no other, forms a complex with silver trifluoroacetate, which crystallizes at  $-78^{\circ}$  and tends to reduce the

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electrophilic activity of the silver salt. Nevertheless our reaction seems useful in that it allows a one-stage preparation of authentic samples of simple and bridged cyclohepta-1,4-dienes which are difficult to obtain by conventional methods. In any new experiments the analogy of benzyne and 2-methylallyl cation reactivity may serve as a useful guide to the yields to be expected. We also draw attention to the general utility of silver trifluoroacetate-isopentane as an electrophilic system, which permits the generation of carbonium ions on a preparative scale.<sup>†</sup>

## EXPERIMENTAL

The products of the cycloadditions were analysed by g.l.c. (Griffin F.I.D. gas chromatograph) on a BB'-oxydipropiononitrile column (10 ft), unless otherwise stated, at 60° and by comparing the peak area of the cycloadduct  $C_{10}H_{14}$  with that from a known quantity of t-butylbenzene. The molar response of the standard  $(C_{10}H_{14})$  was taken to be the same as that of the cycloadduct. Independent experiments with t-butylbenzene and cyclopentadiene dimer ( $C_{10}H_{12}$ ) indicated an error of  $\pm 5\%$ .

Materials .--- Commercial silver trifluoroacetate was recrystallized from diethyl ether. Silver 3,5-dinitrobenzoate was prepared by our general procedure.1a,9

Silver trifluoroacetate dispersed on Diatomite. Silver trifluoroacetate (5 g) was dissolved in diethyl ether (200 ml) and G-Cel (20 g; 60-80 mesh) was stirred into the solution. The solution was evaporated at low pressure and the remaining solid stored in the dark.

Silver carbonate dispersed on molecular sieve 3A.10 Silver nitrate (5.66 g) and sodium carbonate (1.7 g) were added to a stirred suspension of molecular sieve 3A (15 g) in water (100 ml). After complete addition, the solid was filtered off, washed with water, acetone, and ether, dried in vacuo, and stored in the dark.

Amberlite IR-120,  $Ag^+$  form. Amberlite IR-120 (50 ml) was converted into the Na<sup>+</sup> form by elution with 0·1N-NaOH in a column and washing to neutrality. Silver ion (0.025M) was then introduced by repeated elution with silver nitrate solution, the deposition being monitored titrimetrically.

Allyl Trifluoroacetate.<sup>11</sup>—Allyl alcohol (9 ml, 0.083 mol) and trifluoroacetic acid (7.5 ml, 0.1 mol) were refluxed for 2 h with a catalytic amount of sulphuric acid. The resulting solution was washed with aqueous sodium hydrogen carbonate, dried (MgSO<sub>4</sub>) and distilled (b.p. 66° at 760 mmHg) to afford allyl trifluoroacetate (80%),  $\tau$  3.7-4.4 (1H, complex), 4.58 (1H, s), 4.63 (1H, d, J 6 Hz), and 5.22 (2H, d, J 6 Hz).

2-Methylallyl Trifluoroacetate.11-Silver trifluoroacetate (10 g, 0.05 mol) and 2-methylallyl iodide <sup>1a</sup> (6 ml, 0.05 mol) were stirred in ether (50 ml) for 4 h. The mixture was filtered, the solvent evaporated, and the residue distilled (b.p. 85°) to afford 2-methylallyl trifluoroacetate (70%)  $\tau$  (CCl<sub>4</sub>) 4.92 (2H, complex d), 5.21 (2H, s), and 8.2 (3H, s);

7 R. Hoffmann and R. B. Woodward, J. Amer. Chem. Soc., 1965, 87, 2046.

8 G. F. P. Kernaghan and H. M. R. Hoffmann, J. Amer. Chem. Soc., 1970, 92, 6988.

<sup>9</sup> H. M. R. Hoffmann, J. Chem. Soc., 1965, 6748.
 <sup>10</sup> Cf. M. Fétizon and M. Golfier, Compt. rend., 1968, 267, 900.
 <sup>11</sup> H. W. Coover, jun., and J. B. Dickey, U.S.P. 2,759,912 (Chem. Abs., 1957, 51, 2327f).

<sup>\*</sup> Interestingly, at -78 °C (at which temperature benzyne must be far more stable) the cycloadduct with butadiene is formed in 90% yield; see R. W. Atkin and C. W. Rees, *Chem. Comm.*, 1969, 152, footnote.

<sup>†</sup> We have used the same system to generate vinylic cations such as  $\alpha$ -styryl cations from the corresponding bromides at room temperature. Consistent with our suggested mechanism, the vinylic trifluoroacetates are formed with retention of con-figuration,<sup>8</sup> *i.e.* on the surface of the silver salt.

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 $\nu_{\text{max.}}$  1780 (C=O) and 1675 cm<sup>-1</sup> (C=C);  $R_t$  (isopentane standard at 60°) 1.5. When isopentane was used instead of diethyl ether as the solvent, 2-methylallyl trifluoroacetate (50%), trifluoroacetic acid, and polymer were formed.

General Cycloaddition Procedure.—(a) In liquid sulphur dioxide. Silver trifluoroacetate (2.75 g, 0.0125 mol), 2-methylallyl iodide (1.5 ml, 0.0125 mol) and conjugated diene (0.0375 mol) were stirred in liquid sulphur dioxide (100 ml) at  $-78^{\circ}$  for 6 h. The mixture was filtered and extracted with isopentane (3 × 100 ml) previously cooled to  $-25^{\circ}$ . The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate, and the bulk of the solvent was removed at reduced pressure. The resulting solution was analysed by g.l.c. after addition of a standard amount (0.50 ml) of t-butylbenzene.

(b) In hydrocarbon solvents. Silver trifluoroacetate, 2-methylallyl iodide, and diene in quantities as above were stirred in the solvent (50 ml) for 6 h at  $-78^{\circ}$ . Powdered solid potassium hydroxide (5 g) was added and the resulting solution was allowed to warm slowly to room temperature. The solution was filtered and (in the case of isopentane) the solvent was removed. The products were analysed as before. In order to study the effect of trifluoroacetic acid on the reactants, 2-methylallyl iodide, cyclohexadiene, and 2-methylbut-2-ene were treated with the acid in carbon tetrachloride. To simulate the slow and homogeneous formation of the acid as occurs in the cycloaddition, trifluoroacetic acid was dissolved in carbon tetrachloride and added slowly with vigorous stirring. After 1 h at room temperature, 2-methylallyl iodide was unchanged, and cyclohexadiene had decreased by 25% and the olefin by 77%.

1-Methylcyclohepta-1,4-diene (3a).-The cycloaddition of the 2-methylallyl cation to butadiene in isopentane solvent gave a new peak in 6% yield [ $R_t$  0.35 with respect to t-buty]benzene on 1,2,3-tris-( $\beta$ -cyanoethoxy)propane (10 ft) at 60°], which was identified as 1-methylcyclohepta-1,4-diene (3a) by g.l.c. comparison on several columns with an authentic sample, prepared as follows. Cyclohept-4-enemethanol 5a was converted into the tosylate (a yellow oil), which was treated with ca. 1.2 mol. equiv. of 0.5M-potassium t-butoxide in dimethyl sulphoxide for 1 h.50 The resulting solution was distributed between isopentane and icewater and the aqueous solution was extracted with more isopentane (3 imes 50 ml). The hydrocarbon layers were combined, washed with water, and dried  $(MgSO_4)$ . Evaporation left 4-methylenecycloheptene (3b),  $\tau$  4.2br (2H, s), 5.35 (2H, s), and 7.8br (8H, s), the spectrum being identical to one provided by Dr. R. W. Thies.5b G.l.c. [1,2,3-tris- $(\beta$ -cyanoethoxy)propane (10 ft) at 60°] revealed a major peak (95%) ( $R_t$  0.245 relative to t-butylbenzene) and a minor one (5%)  $(R_t \ 0.35)$  formed by base-catalysed isomerization of (3b).<sup>12</sup> On treatment with acid [CF<sub>3</sub>CO<sub>3</sub>H (0.3 ml) in isopentane (10 ml) and diene (0.5 ml) the minor peak grew at the expense of the major one, the ratio being ca. 4:3 in favour of the new peak after 48 h. Independently, the isomerization of (3b) and (3a) could be followed by n.m.r., which showed a decrease of the peak

at  $\tau$  5.35 [2H, s, (3b) methylene] and a new peak at 8.4 [3H, s, (3a) methyl].

Reaction of 2-Methylallyl Cation with Isoprene and 2,3-Dimethylbutadiene.--The reaction of 2-methylallyl cation with isoprene in isopentane at 78° gave two new products, (A) (1.8%).  $R_t$  0.27 with respect to t-butylbenzene) and (B) (2.9%,  $R_t$  0.33), as well as traces of other compounds, shown by control experiments to be formed via acid-catalysed dimerization of isoprene 13 with trifluoroacetic acid in isopentane. The mixture was hydrogenated (40°; 4-6 atm; 9-17 h; 10% Pd-CaCO<sub>3</sub>) and reexamined on various g.l.c. columns. While the hydrogenation of compounds (A) and (B) proved difficult owing to the small amount of product formed, their proportions had definitely decreased after 17 h, and altogether seven new peaks had appeared [Apiezon L (4 m) at 110°]. Of these peaks two were shown by control experiments to be formed by hydrogenation of 2-methylallyl iodide and trifluoroacetate and four by hydrogenation of impurities in isoprene; the seventh (small) had a retention index <sup>14</sup>  $I_{110}^{AP}$ . of 950 (retention index of authentic cis- and trans-1,4-dimethylcyclohepta-1,4-diene  $I_{110}^{AP} = 952^{15}$ ).

The reaction of 2,3-dimethylbutadiene with the 2-methylallyl cation gave a new peak (4% yield) ( $R_t$  0.54 with respect to t-butylbenzene) and two further unknown compounds (*ca.* 1%) ( $R_t$  0.73 and 1.0), which were shown to be formed by acid-catalysed dimerization of 2,3-dimethylbutadiene.

Bicyclo[3,2,1]octa-2,6-diene (8).<sup>16</sup>—Allyl iodide (3 ml, 0.0125 mol), cyclopentadiene (3.1 ml, 0.0375 mol), and silver trifluoroacetate (3 g, 0.014 mol) were stirred in isopentane (20 ml) for 6 h at  $-78^{\circ}$ . Powdered potassium hydroxide was added and the suspension was then allowed to warm to room temperature. After filtration and removal of the solvent, the solution was examined by g.l.c., showing a new peak as a shoulder on that due to the remaining allyl iodide. After removal of the allyl iodide together with allyl trifluoroacetate (70%) by treatment with diethylamine (3 × 1 ml) followed each time by washing with 0.1N-hydrochloric acid (20 ml), bicyclo-[3,2,1]octa-2,6-diene (8) (6%) was identified by comparison on several columns with an authentic sample, furnished by Dr. J. M. Brown.

Silver-Butadiene Complex.—On stirring butadiene and silver trifluoroacetate in isopentane at room temperature, the silver salt slowly dissolved. On cooling to  $-78^{\circ}$ , a white solid separated which was filtered off and dried *in* vacuo. No darkening of the solid occurred on exposure to light for periods of up to 3 weeks (AgO<sub>2</sub>C·CF<sub>3</sub> darkens slowly within hours),  $\lambda_{max}$  214 nm ( $\pi$ - $\pi^*$ ) (butadiene 217 nm). Treatment with aqueous sodium iodide released butadiene.<sup>3</sup>

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