

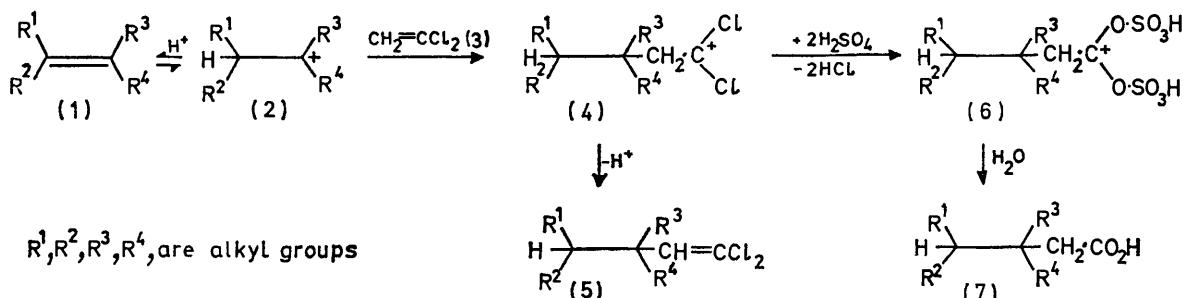
Reaction of Norbornadiene with a Mixture of 1,1-Dichloroethylene, Sulphuric Acid, and Boron Trifluoride—Ether Complex

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The reaction of norbornadiene with a mixture of 1,1-dichloroethylene, sulphuric acid, and boron trifluoride—ether does not give the expected dicarboxylic acids. The major product is a neutral fraction containing tricyclo[2.2.1.0^{2,6}]heptan-3-yl chloride, 2-exo,7-syn-dichloronorbornane, 2-exo,5-endo-dichloronorbornane, and 2-exo,5-exo-dichloronorbornane. An additional product is an acid lactone thought to be 5-exo-carboxymethyl-6-endo-hydroxynorbornan-2-endo-ylacetolactone. The formation of the dichlorides is suggested to involve the norbornenyl and chloronorbornyl carbonium ions; other potential sources of these ions lead to similar mixtures of dichlorides. The neutral fraction from the reaction with norbornene contains some 2-exo-chloronorbornane.

A CONVENIENT method for the conversion of olefins (1) into carboxylic acids of type (7) has been developed by Bott.¹ This involves treatment of the olefin (1) with concentrated sulphuric acid in the presence of boron trifluoride; the initial product is the carbonium ion (2), which adds to 1,1-dichloroethylene to give the chlorine-substituted carbonium ion (4). This ion (4) is then believed to achieve stability by rapidly exchanging its

dienes, and with the object of preparing the dicarboxylic acids (8), the reaction of norbornadiene (9) with 1,1-dichloroethylene (3) in the presence of concentrated sulphuric acid containing boron trifluoride—ether complex was investigated. Acidic and neutral products, in the ratio of *ca* 1 : 4, were produced. The neutral fraction consisted of five products (see Table for proportions), four of which [(10)—(13)] were isolated by

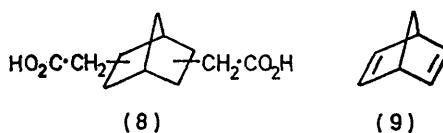


chlorine atoms for sulphate groups to afford the ion (6). In the work-up, hydrolysis of this ion (6) leads to the carboxylic acid (7). The dichloro-olefin (5) may be formed as a by-product as a result of the loss of a proton by (4). Primary, secondary, and tertiary alcohols, halides, or esters may also be used in this reaction instead of the olefin (1), as alternative sources of the carbonium ion (2).

In the hope that the reaction could be extended to

¹ K. Bott and H. Hellman, 'Newer Methods in Preparative Organic Chemistry,' vol. VI, ed. W. Forest, Academic Press, New York and London, p. 67, and references cited therein.

preparative g.l.c. Tricyclo[2.2.1.0^{2,6}]heptan-3-yl chloride (10) was identical with an authentic specimen,



having properties appreciably different from those of the *endo*-norbornenyl chloride (14a).² The dichlorides (11)

² W. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *J. Org. Chem.*, 1965, **30**, 2886.

and (12) had properties consistent with those recorded.^{3,4} The n.m.r. spectra of (11) and (13) were virtually identical with those of the corresponding dibromides.⁵ All compounds had mass spectra consistent with their structures. The fifth component could not be obtained in quantities sufficient for identification, but the molecular ion in its mass spectrum corresponded to C₇H₁₀Cl₂.

Reactants and products in the reaction of 1,1-dichloroethylene (3) with norbornadiene (9) and related carbonium ion sources

Reactants				Products								
Carbonium ion source	No.	(3)	H ₂ SO ₄ (98%)	BF ₃ -Et ₂ O	(22)	Neutral fraction (g)	Proportions (%) of dichlorides in neutral fraction	(10)	(11)	(12)	(13)	unknown
ion source	g	(g)	(ml)	(ml)	(g)	(g)						
(9)	9	19.4	10	3	4.5	12.7	3.4	18.5	34.5	40.1	3.5	
(10)	12.7	19.4	10	3	0.0	10.0	3.2	14.0	35.3	43.5	4.0	
(14a)	12.7	19.4	10	3	0.3	9.4	3.3	15.3	34.6	43.8	3.0	
(14b)	10.7	19.4	10	3	0.6	7.4	2.1	16.0	34.5	43.4	4.0	
(14c)	15.6	19.4	10	3	1.1	6.2	1.8	17.0	34.3	43.7	3.2	

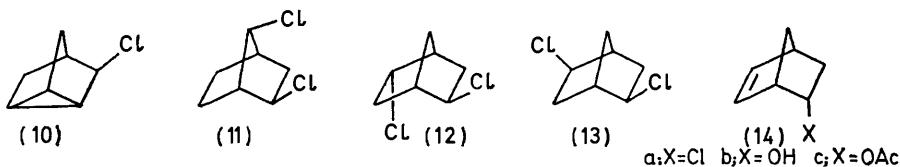
suggesting that it was also a dichloronorbornane. It is not a 2,3-dichloronorbornane, since its g.l.c. retention time did not correspond with those of authentic specimens.⁴

The first step of reaction is presumably protonation, to give the norbornenylum ion. Since this is a stabilised carbonium ion,⁶ its reaction with 1,1-dichloroethylene (3) is likely to be relatively slow; protonation

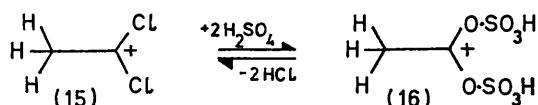
affords 15% of 1-chloro-3,5,7-trimethyladamantane, presumably as a result of capture, by chloride ion, of the comparatively stable 3,5,7-trimethyl-1-adamantylum carbonium ion.⁷

Of the two possible intermediates (10) and (14a), the former is likely to predominate since it is known to be increasingly favoured, over (14a), as a product of

additions of hydrogen chloride to norbornadiene (9) in more polar solvents.⁸ Also, the *endo*-chloride (14a) is known to be isomerised to (10) by Lewis acid catalysts.⁹ Supporting evidence for the intermediacy of (10) and (14a) is that they both give similar mixtures of dichlorides (11)–(13) in this reaction (see Table). Similar mixtures are also formed when the *endo*-alcohol (14b) and acetate (14c), potential precursors of the

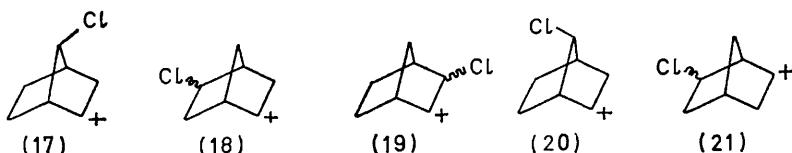


of (3) therefore occurs in preference to give the carbonium ion (15), and subsequently (16). This process



involves the production of chloride ion which, being a better nucleophile than 1,1-dichloroethylene (3), readily

norbornenylum ion, are used in the reaction. Protonation of (10) or (14a) should give a chloronorbornylium ion. Knowledge of the norbornylium ion⁶ suggests, that under the conditions where it is generated, the carbon atoms of the chloronorbornylium ion are likely to be indistinguishable as a result of the possibility of various Wagner-Meerwein rearrangements, 6,2-hydride shifts, and 3,2-hydride shifts. The products (11) and [(12) + (13)] may be considered to be derived from the



captures the norbornenylum ion to give a mixture of chlorides (10) and (14a). Consistent with this suggestion is the report that the corresponding reaction of 1-hydroxy-(or acetoxy)-3,5,7-trimethyladamantane

³ J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, 1954, **76**, 5692.

⁴ R. Hüttel, H. Reinheimer, and K. Nowak, *Chem. Ber.*, 1968, **101**, 3761.

⁵ D. Marshall, P. Reynolds-Warnhoff, E. W. Warnhoff, and J. R. Robinson, *Canad. J. Chem.*, 1971, **49**, 885.

open ions (17) and (18), respectively. Products derived from capture of the ions (19)–(21) by chloride ions were not detected, and it seems safe to assume

⁶ G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 1970, **92**, 4627.

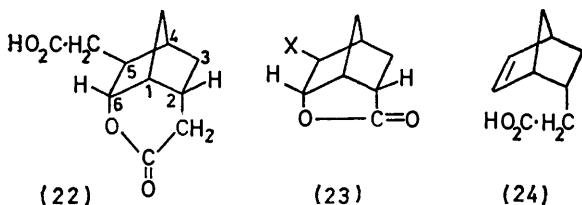
⁷ K. Bott, *Chem. Ber.*, 1968, **101**, 564.

⁸ T. C. Morrell and B. E. Greenwald, *J. Org. Chem.*, 1971, **36**, 2769.

⁹ J. D. Roberts and W. Bennett, *J. Amer. Chem. Soc.*, 1954, **76**, 4623.

that they are not formed to any appreciable extent. Therefore it is reasonable to suggest that in these ions the position of the chlorine atom relative to the carbonium ion centre is such that it produces greater inductive destabilisation than in (17) and (18). Similar inductive destabilisation was invoked by Fry and Farnham to explain the virtually exclusive formation of 1,3-*exo*-dichlorobornornane in the hydrochlorination of 1-chloronorbornene.¹⁰ Support for the proposed mechanism for product formation was provided by the observation that the products (10)–(13) are formed in similar proportions by the addition of hydrogen chloride to norbornadiene (9) in methylene chloride containing sulphuric acid and boron trifluoride–ether.

The acidic product of the reaction between 1,1-dichloroethylene (3) and norbornadiene (9) was shown by i.r. evidence to contain both a carboxy-group and an ester or lactone carbonyl. Proof of a lactone structure was provided by the recovery of the compound unchanged after refluxing with sodium hydroxide solution followed by acidification. Structure (22) is favoured since the pattern in the n.m.r. spectrum for the presumed H-6-*exo* is almost identical with that of H-6-*exo* in related compounds (23).¹¹ Additionally, the lactone (22) is formed in good yield by reaction of the *endo*-acetic acid (24) (prepared¹² by Diels-Alder addition of vinyl acetic acid to cyclopentadiene) with 1,1-dichloroethylene (3). Although the i.r. spectrum of (22) shows lactone carbonyl absorption at 1775 cm⁻¹, which is more appropriate for a γ -lactone,¹³ it is at a lower frequency than for γ -lactones of type (23), which absorb in the range 1779–1790 cm⁻¹.¹¹ The rigidity of the ring system in (23) clearly results in the γ -lactone carbonyl frequency being higher than usual, and therefore



the unusual position of the proposed δ -lactone carbonyl absorption of (22) is appropriate.

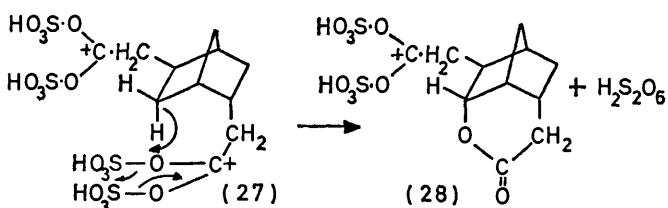
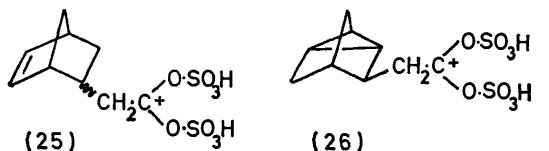
The formation of (22) could involve capture of the norbornenylium ion by 1,1-dichloroethylene (3) followed by exchange with sulphuric acid leading to the ions (25) and (26). Similar reactions of these ions could lead to (27), which could break down as indicated to give (28), the obvious precursor of (22). Since (22) is the sole acidic product derived from (9), the various stages of reaction leading to (28) and other possible acidic products must be reversible, so that (28), which must have particular stability, is the only intermediate that survives to give product. The acid fraction, in addition

¹⁰ A. J. Fry and W. B. Farnham, *Tetrahedron Letters*, 1968, 3345; *J. Org. Chem.*, 1969, **34**, 2314.

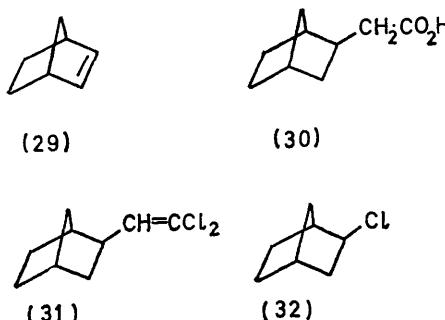
¹¹ K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Amer. Chem. Soc.*, 1967, **89**, 2401.

¹² K. Alder and E. Windemuth, *Ber.*, 1938, **71**, 1939.

to (22), contained an appreciable quantity of acetic acid. This would be derived from hydrolysis of (16) and



substantiates the suggestion that the conversion (15) → (16) is the source of hydrogen chloride for the formation of products (10)–(13).



The reaction of 1,1-dichloroethylene (3) with norbornene (29) is reported to give *exo*-norbornylacetic acid (30) together with *exo*-norbornylvinylidene chloride (31).¹⁴ When the reaction was repeated and the acidic and neutral materials carefully separated, the neutral materials were found to consist of (31) (24.4%) and *exo*-norbornyl chloride (32) (19%). The norbornylum ion is in this reaction largely captured by 1,1-dichloroethylene (3), leading to (30) and (31), rather than by chloride ion to give (32). This contrasts with the chloronorbornylum ion derived from (9), (10), or (14a), for which capture by chloride ion is favoured. These results can be rationalised on the basis that the presence of a chlorine atom in (10) and (14a), and consequent electron withdrawal by chlorine, makes protonation of the ring system more difficult than of norbornene (29). Hence protonation of 1,1-dichloroethylene (3) and consequent production of chloride ions is more favoured than in the reaction of norbornene (29).

EXPERIMENTAL

N.m.r. spectra (90 MHz) were measured for 10% solutions in carbon tetrachloride with an HFX-90 Bruker

¹³ L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958, p. 179.

¹⁴ K. Bott and H. Hellman, *Angew. Chem. Internat. Edn.*, 1966, **5**, 870; K. Bott, *Chem. Ber.*, 1967, **100**, 978.

spectrometer. I.r. spectral data were recorded with a Perkin-Elmer 257 grating spectrometer. Mass spectral data were recorded with an A.E.I. MS30 instrument run at low resolution.

Reaction of 1,1-Dichloroethylene (3) with Norbornadiene (9) and Related Compounds [(10) and (14a—c)] (cf. refs. 1 and 14).—The olefin and 1,1-dichloroethylene (3) (2 mol. equiv.) were added dropwise during 4 h to a well-stirred mixture of 98% sulphuric acid and boron trifluoride-diethyl ether maintained at 5—16°. Stirring was then continued for 1 h at room temperature; the mixture was then hydrolysed by cautious addition of crushed ice, and made alkaline with aqueous sodium hydroxide (20%). After cooling to room temperature the neutral products were extracted with ether (3 × 250 ml). The extracts were washed with water, dried ($MgSO_4$), and evaporated, and the neutral products were purified by distillation. The alkaline solution was acidified with dilute sulphuric acid and the acidic products were isolated, by extraction with ether, in a manner similar to that for the neutral components. The Table records the proportions and quantities of reactants and products. Tricyclo[2.2.1.0^{2,6}]heptan-3-yl chloride (10),² norborn-5-en-2-yl chloride (14a),² norborn-5-en-2-yl acetate (14c),^{15,16} and norborn-5-en-2-yl alcohol (14b)^{18,17} used in the reactions had >90% *endo* stereochemistry and were prepared by the reported methods. The proportions of dichlorides in the neutral fractions were determined by g.l.c. analysis at 100° [Perkin-Elmer F11 gas chromatograph fitted with a flame ionisation detector and a 2 m × 1/8 in column of 5% Carbowax 20M/T.P.A. on A.W.-D.M.C.S. Chromosorb G (80—90 mesh)]. The following products were isolated by preparative g.l.c. of the neutral fractions [Varian A-700 series chromatograph fitted with a 1 m × 1/4 in column of 5% Carbowax 20M/T.P.A. on A.W.-D.M.C.S. Chromosorb G (80—100 mesh)]: (i) tricyclo[2.2.1.0^{2,6}]heptan-3-yl chloride (10), identical with an authentic sample;² (ii) 2-*exo*,7-*syn*-dichloronorbornane (11), b.p. 70—72° at 0·05 mmHg, n_{D}^{25} 1·5083, m.p. 36—38° (lit.,³ m.p. 36—38°, b.p. 97—110° at 11 mmHg) (Found: C, 51·3; H, 6·15. Calc. for $C_7H_{10}Cl_2$: C, 50·9; H, 6·0%), τ 6·4 (*t*, H-2-*endo*) and 5·49 (*m*, H-7-*anti*) [$J(2\text{-}endo,3\text{-}endo)$ = $J(2\text{-}endo,3\text{-}exo)$ = 6 Hz] (the spectrum was virtually identical with that of 2-*exo*,7-*syn*-dibromonorbornane⁵), *m/e* 164 (M^+), 129, 102, 93, 91, 79, 77, and 67, i.r. as reported;³ (iii) unknown compound $C_7H_{10}Cl_2$, *m/e* 164 (M^+), 129, 102, 93, 88, 79, and 67, g.l.c. retention time different from those of the 2,3-dichloronorbornanes;⁴ (iv) 2-*exo*,5-*endo*-dichloronorbornane (12), b.p. 67—70° at 0·5 mmHg, n_{D}^{25} 1·5091 (Found: C, 51·25; H, 6·0; Cl, 42·65. $C_7H_{10}Cl_2$ requires C, 50·9; H, 6·05; Cl, 43·05%), τ 6·05 (*m*, H-2-*endo* and -5-*exo*) and 7·35 (*octet*, H-3-*exo*), [$J(2\text{-}endo,7\text{-}syn)$ 2, $J(2\text{-}endo,3\text{-}endo)$ 7·5, $J(2\text{-}endo,3\text{-}exo)$ 7·1, $J(3\text{-}exo,3\text{-}endo)$ 14·7, $J(3\text{-}exo,4\text{-}2\text{-}1\text{ Hz})$] (the spectrum was virtually identical with that of 2-*exo*,5-*endo*-dibromonorbornane⁵), *m/e* 164 (M^+), 129, 102, 93, 91, 79, 77, and 67; (v) 2-*exo*,5-*exo*-dichloronorbornane (13), m.p. 68—69° (lit.,⁴ 68—70°) (Found: C, 51·05; H, 6·2; Cl, 42·75. Calc. for $C_7H_{10}Cl_2$: C, 50·9; H, 6·05; Cl, 43·05%), n.m.r. identical with that reported,⁴ *m/e* 164 (M^+), 129, 102, 93, 92, 79, 77, and 67.

¹⁵ J. D. Roberts, E. R. Trumbull, jun., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 1950, **72**, 3116.

The acid fractions were distilled to give acetic acid (*ca.* 1 g) and 5-exo-carboxymethyl-6-endo-hydroxynorbornan-2-endo-ylacetolactone (22), b.p. 80—86° at 0·1 mmHg, n_{D}^{25} 1·4805 (Found: C, 62·5; H, 7·0. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·65%), τ 5·89br (*d*, H-6-*exo*) [$J(1,6\text{-}exo)$ 1, $J(5\text{-}endo,6)$ 5 Hz], *m/e* 210 (M^+), 152 ($M^+ - CH_2CO_2$), 123, 108, and 92, ν_{max} 1775 (C=O of lactone), 1740—1680 (C=O of acid), and 3700—3015 cm⁻¹ (OH of acid).

Reaction of 1,1-Dichloroethylene (3) with Norbornene (29) (cf. ref. 12).—The procedure used for (9) and related compounds, applied to norbornene (29) (4·7 g), 1,1-dichloroethylene (3) (10 g), sulphuric acid (10 ml of 98%), and boron trifluoride-ether (3 ml), afforded 2-*exo*-chloronorbornane (32) (0·8 g), b.p. 62—64° at 10 mmHg, n_{D}^{25} 1·4937 (lit.,^{5,18} b.p. 80—81° at 50 mmHg, n_{D}^{25} 1·4832) (Found: C, 64·2; H, 8·6; Cl, 27·2. Calc. for $C_9H_{11}Cl$: C, 64·4; H, 8·45; Cl, 27·2%), n.m.r. spectrum identical with that reported.^{5,18} Also isolated were *exo*-norbornylvinylidene chloride (31) (1 g) and *exo*-norbornylacetic acid (30) (4·2 g) having properties identical with those reported.¹⁴

Reaction of 1,1-Dichloroethylene (3) with Norborn-5-en-2-endo-ylacetic Acid (24).—The procedure used for (9) and related compounds, applied to the acid (24)¹² (8 g), 1,1-dichloroethylene (3) (9·7 g), sulphuric acid (20 ml of 98%), and boron trifluoride-ether (3 ml), afforded the acid lactone (22) (6 g) and acetic acid (2 g).

Addition of Hydrogen Chloride to Norbornadiene (9).—Norbornadiene (9) (2 g) dissolved in methylene chloride (10 ml) was added slowly (*ca.* 1·5 h) to a cooled solution of sulphuric acid (10 ml of 98%) and boron trifluoride-ether (3 ml). Hydrogen chloride gas was then bubbled through the cooled solution for 0·5 h. The resulting mixture was cautiously hydrolysed by addition of ice (*ca.* 20 g.), aqueous sodium hydroxide (20 ml of 20%) was added, and the resultant suspension was extracted with ether (3 × 100 ml). The extracts were combined, washed with water, dried ($MgSO_4$), and evaporated. G.l.c. analysis of the crude product indicated that the products were the same and were in the same proportions as those in the neutral fraction from the reaction of norbornadiene (9) with 1,1-dichloroethylene (3).

Attempted Hydrolysis of the Acid Lactone (22).—The lactone (22) (1·0 g) dissolved in aqueous sodium hydroxide (10 ml of 20%) was boiled at reflux for 12 h. Extraction of the cooled solution with ether (3 × 25 ml) afforded no neutral material. The alkaline solution was then acidified with dilute sulphuric acid and extracted with ether (3 × 50 ml). The extracts were washed with water, dried ($MgSO_4$), and evaporated to afford a pale yellow liquid (0·9 g) having properties identical with those of starting material (22). Similar results were obtained when stronger solutions of ethanolic sodium hydroxide were used.

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[3/856 Received, 25th April, 1973]

¹⁶ D. I. Davies, D. J. A. Pearce, and E. C. Dart, *J.C.S. Perkin I*, 1973, 433.

¹⁷ K. Alder and H. F. Rickert, *Annalen*, 1939, **543**, 1.

¹⁸ M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 4293.