of **14** from longifolene and the addition of halogens to camphene, the isoprenolog of **1**, leading to tricyclene derivatives.

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Syntheses Employing Hexamethyl(Dewar benzene). Reactions of Methyl-Substituted Carbonium Ions with Triethylamine[1]

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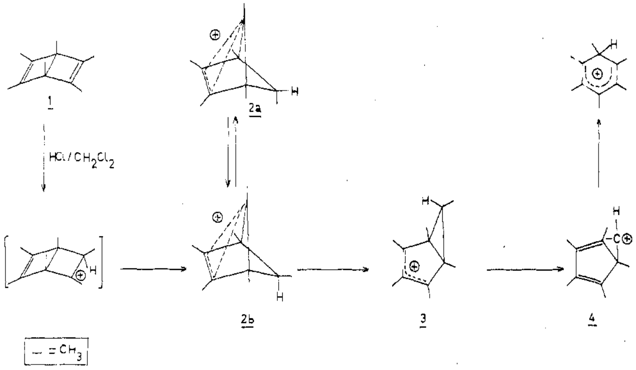
Syntheses of 1,2,3,5,6-pentamethyl-4-methylenebicyclo[3.1.0]hex-2-ene (**5**), 1,2,4,5,6-pentamethyl-3-methylenetricyclo[$2.2.0.0^{2,6}$]hexane (**8**), 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[$3.1.0.0^{2,6}$]hexane (**9**), and 5-α-chloroethyl-1,2,4,5-tetramethyl-3-methylenecyclopentene (**16**) are reported. These involve proton abstraction by triethylamine from the corresponding carbonium ions. The proton abstraction is proposed to be a kinetically controlled process occurring at the methyl group adjacent to the carbon atom bearing the highest positive charge.

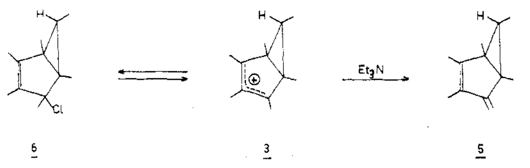
Reactions of hexamethyl(Dewar benzene) (**1**) with acids have been the subject of many investigations in recent years.[2,3] Protonation of **1** followed by rearrangement will give isomers of **1** after subsequent proton abstraction. Triethylamine appeared to be particularly useful for performing these proton abstractions. Some other carbonium ions originating from **1** have been treated in the same way and the low-temperature abstraction of a proton from a methyl-substituted carbonium ion with triethylamine seems to be generally applicable as a good synthetic method for preparing strained compounds with exocyclic methylene groups. The results of this reaction are presented below.

Results and Discussion

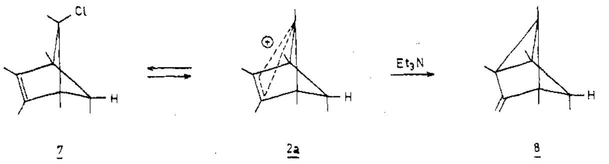
It has been shown that the reaction path of **1** with HCl followed by subsequent isomerization is as follows.[2d]



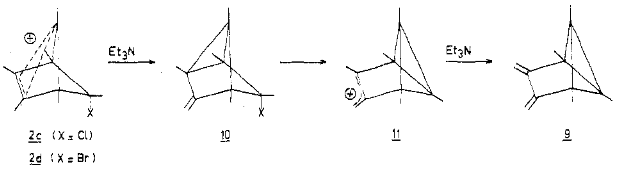
The homofulvene **5**, which is an isomer of **1**, was prepared *via* reaction of **1** with HCl at −40° to give **6**. Compound **6** will dissociate to give cation **3**, which then reacts with triethylamine with loss of a proton. The homofulvene **5** was prepared previously by a photochemical isomerization of **1**,[4] and also by quenching of a strongly acidic solution of **3** with sodium bicarbonate in methanol.[5] The stereochemistry of **5**, once supposed to be exo-H,[6] is accepted now to be endo-H. The assignment is based on comparison[5,7] of the pmr chemical shifts of **5** and the related ion **3** with those of the homofulvene and the cation with the inverted H and CH_3 configuration.[8]

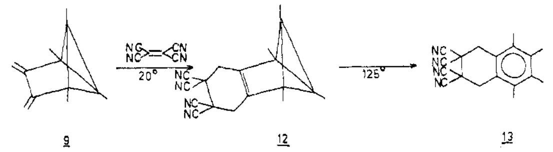


For the preparation of a tricyclic isomer of **1**, compound **8**, the following procedure was developed. The cation mixture **2a,b** (3:1 in equilibrium[3a]), obtained from reaction of **1** with HCl in methylene chloride at −80°,[2d] was poured into triethylamine at −80°. The pmr spectrum of this mixture indicates that **7**[2d] is formed first; subsequently **7** will dissociate to give ion **2a** and triethylamine will then abstract a proton from the methyl group adjacent to the carbon atom bearing the highest positive charge[9] in ion **2a**.



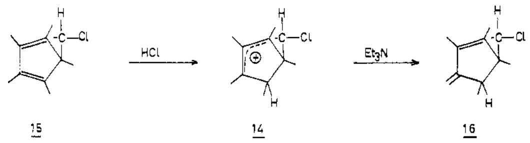
Another application of the reaction of methyl-substituted carbonium ions with triethylamine is found in the synthesis of **9**. The cations **2c** and **2d**, formed from the reaction of **1** with chlorine and bromine, respectively,[9] give **9** upon proton abstraction with triethylamine. This product can be accounted for by assuming that the proton abstraction to give **10** occurs in the same way as with **2a**. The intermediate **10** will presumably dissociate to give cation **11**, which then undergoes another proton abstraction to give **9**. Compound **9** was obtained also by pouring a solution of dication $(CCH_3)_6^{2+}$ in a triethylamine solution at low temperature.[10] Structure **9** was assigned on the basis of





the spectra and the Diels–Alder reaction of **9** with tetracyanoethylene to give **12**, which in turn isomerized to **13** on heating.

The role of the positive charge in determining the site of the proton abstraction is shown by the reactivity of ions **2a**, **2c**, and **2d**. It is suggested by the products that the reactions are kinetically controlled; otherwise thermodynamically favored[9] bicyclic products would have formed. The kinetic control of proton abstraction from methyl-substituted carbonium ions is illustrated by the reactivity of cation **14**. Cation **14** is obtained on protonation of **15**, which is itself formed by reaction of **1** with HCl at room temperature. Triethylamine did not give the reverse reaction with **14**, *i.e.*, proton abstraction yielding **15**; instead the amine abstracted a methyl proton to give **16**. Compound **16** was observed previously[11] as a product of the reaction of compound **8** with HCl at low temperature. The isomerization of **16** to **15** occurs almost instantaneously at room temperature on addition of a trace of acid. This behavior of **16** shows **15** to be the thermodynamically more stable isomer. Thus, proton abstraction from **14** has to be a kinetically controlled process. Presumably this is general for low-temperature proton abstraction from methyl-substituted carbonium ions with triethylamine.



Experimental Section

Proton magnetic resonance spectra were recorded at 60 MHz using a Varian A-60D spectrometer. Chemical shifts are calculated relative to internal TMS at δ 0. Natural abundance carbon-13 nuclear magnetic resonance spectra were obtained with a Varian XL-100 spectrometer operating at 25.2 MHz. Spectra were recorded using Fourier transform and were proton-noise decoupled. Chemical shifts were calculated relative to external (capillary) TMS. Mass spectra were determined with an AEI MS 902 mass spectrometer and ir spectra were obtained with use of a Perkin-Elmer 257 spectrometer. Only representative peaks are given. Uv spectra were measured with a Beckman DB-G spectrophotometer.

1,2,3,5,6-Pentamethyl-4-methylenebicyclo[3.1.0]hex-2-ene (5). In a 250-ml three-necked bottle equipped with a mechanical stirrer, 3.20 g (0.02 mol) of hexamethyl(Dewar benzene) was dissolved in 60 ml of methylene chloride. The solution was cooled to −40° and 1.80 g (0.05 mol) of dry hydrogen chloride gas was introduced. A solution of 10.0 g (0.1 mol) of triethylamine in 30 ml of methylene chloride was added rapidly with stirring. The temperature of the reaction mixture was allowed to rise to 20° while stirring was continued for 2 hr, after which the solvent was evaporated and pentane (50 ml) and water (500 ml) were added. The organic layer was separated, washed with water until the smell of triethylamine had disappeared, and dried over sodium sulfate. The pentane was evaporated and the crude product was distilled to give a 2.45-g (0.015 mol, 75%) yield of **5**, bp 74–76° (5 mm); it was characterized by its nmr and ir spectra.[7]

1,2,4,5,6-Pentamethyl-3-methylenetricyclo[2.2.0.0^{2,6}]hexane (8). In a 250-ml three-necked bottle equipped with a mechanical stirrer, 3.20 g (0.02 mol) of hexamethyl(Dewar benzene) was dissolved in 60 ml of methylene chloride. The solution was cooled to −80° and 1.80 g (0.05 mol) of dry hydrogen chloride gas was introduced. A solution of 10.0 g (0.1 mol) of triethylamine in methylene chloride at −80° was added rapidly and with stirring from a cooled dropping funnel. The reaction mixture was stirred at −70° for 3 hr and warmed to room temperature over another 3 hr. The solvent was evaporated and pentane (50 ml) and water (500 ml) were added. The organic layer was separated, washed with water until the smell of triethylamine had disappeared, and dried over sodium sulfate. The pentane was evaporated and the crude product was distilled, bp 47.5–48.5° (3.7 mm), to give a 2.55-g (0.016 mol, 80%) yield of **8** as a colorless liquid. An analytically pure sample was obtained by preparative glc (SE-30 column, all temperatures below 200°). Compound **8** is rapidly oxidized upon exposure to the air at room temperature: mass spectrum parent peak at *m/e* 162; ir spectrum *inter alia* 3070 (=CH_2 stretching), 1655 (C=C stretching), and 860 cm^{-1} (=CH_2 out-of-plane deformation); pmr spectrum (CCl_4) δ 4.57 (d, *J* = 0.8 Hz, 1 H), 4.54 (d, *J* = 0.8 Hz, 1 H), 2.01 (q, *J* = 7 Hz, 1 H), 1.33, 1.28, 1.03, 1.00 (s, each 3 H), and 0.86 (d, *J* = 7 Hz, 3 H); cmr spectrum[9] (CH_2Cl_2) peaks at 166.2, 97.4, 47.7, 45.0, 45.0, 27.2, 24.2, 18.5, 9.5, 8.7, 4.7 and 4.3 ppm downfield from external (capillary) TMS.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.5; H, 11.3.

1,2,5,6-Tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (9). In a 250-ml three-necked bottle equipped with a mechanical stirrer, 3.20 g (0.02 mol) of hexamethyl(Dewar benzene) was dissolved in 60 ml of methylene chloride. The solution was cooled to −80° and about 1 equiv of dry chlorine gas was introduced to give a solution of ion **2c**. Alternatively a solution of 4.0 g (0.025 mol) of bromine in 10 ml of methylene chloride was introduced slowly at −80° to give a solution of ion **2d**. The solutions of ions **2c** or **2d** were treated with 4.0 g (0.04 mol) of triethylamine in 10 ml of methylene chloride, which was introduced from a dropping funnel in 15 min with stirring. The temperature of the reaction mixture was not allowed to exceed −70° during the addition and 2 hr thereafter, during which time triethylammonium salt precipitated. After warming to room temperature (over 2 hr), the solvent was evaporated and 50 ml of pentane and 500 ml of water were added. The organic layer was separated, washed with water until the smell of triethylamine had disappeared, and dried over sodium sulfate. The pentane was evaporated, leaving 3.0 g of a crude product, which consisted according to the nmr spectrum of 85% of **9**. Vacuum distillation provided 1.9 g (0.012 mol, 60% yield) of **9**, bp 69–70° (12 mm). The residue contained hexamethylbenzene (0.3 g, 0.002 mol, 10%). An analytically pure sample was obtained by preparative glc (SE-30 column, all temperatures below 150°). Compound **9** is oxidized rapidly upon exposure to the air at room temperature: mass spectrum parent peak at *m/e* 160; ir spectrum *inter alia* 3080 (=CH_2 stretching), 1640 (C=C stretchig), and 865 cm^{-1} (=CH_2 out-of-plane deformation); uv spectrum λ_{max} (ethanol) 204 nm (log ε 3.95) and 250 (3.78); pmr spectrum (CCl_4) δ 5.00 (s, 2 H), 4.53 (s, 2 H), 1.42 (s, 6 H), 1.14 (s, 6 H); cmr spectrum (CH_2Cl_2) peaks at 157.5, 98.7, 47.1, 31.4, 10.0, and 6.0 ppm downfield from external (capillary) TMS.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.2; H, 10.1.

Reaction of 9 with Tetracyanoethylene. Tetracyanoethylene (128 mg, 1.0 mmol) was added as a solid to a stirred solution of 160 mg (1.0 mmol) of **9** in 3 ml of chloroform at room temperature. After 10 min the solvent was evaporated to leave 285 mg (1.0 mmol, 100%) of the adduct **12**. It was purified by crystallization from CCl_4–$CHCl_3$: mass spectrum parent peak at *m/e* 288; *inter alia* 2260 (weak, C≡N) and 1665 cm^{-1} (weak, C=C); pmr ($CDCl_3$) δ 3.12 (s, 4 H), 1.47 (s, 6 H), 1.16 (s, 6 H).

Anal. Calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.5; H, 5.6; N, 19.2.

Pyrolysis of 12. On warming a neat sample of **12** at 125° a reaction took place without melting. The product obtained,[12] **13**, showed a melting point of 230–232°: mass spectrum parent peak at *m/e* 288, base peak at *m/e* 160; ir *inter alia* 2260 (weak, C≡N) and 740 cm^{-1} (ortho-disubstituted benzene); pmr ($CDCl_3$) δ 3.72 (broad s, 4 H), 2.30 (s, 6 H), 2.20 (s, 6 H); uv λ_{max} ($CHCl_3$) 274 nm (log ε 2.60).

Anal. Calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.7; H, 5.7; N, 19.3.

5-α-Chloroethyl-1,2,4,5-tetramethyl-3-methylenecyclopentene (16). In a nmr tube, 100 mg (0.5 mmol) of 1-α-chloroethyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene[2b] (**15**) was dissolved in 0.5 ml of methylene chloride. This solution was cooled to −80° and 180 mg (5 mmol) of dry hydrogen chloride gas was introduced at this temperature to give a solution of cation **14**, which was detected by its pmr spectrum at −80°.[11] The solution of cation **14** was poured with stirring into a mixture of 1.00 g (10 mmol) of triethylamine and 20 ml of methylene chloride at −80°, after which triethylammonium salt precipitated. The reaction mixture was kept at −70° for 1 hr and then warmed up to room temperature. After the solvent was evaporated, 20 ml of pentane and 200 ml of water were added and the organic layer was separated, washed with water until the smell of triethylamine had disappeared, and dried over sodium sulfate. The solvent was evaporated, leaving 95 mg of a yellow liquid, which consisted of 90% **16** (determined by pmr). Upon standing at room temperature **16** rapidly isomerized to **15**: mass spectrum parent peak at m/e 198, 200 (3:1); ir *inter alia* 3100 ($=CH_2$ stretching), 1625 ($C=C$ stretching), and 880 cm^{-1} ($=CH_2$ out-of plane deformation); pmr (CCl_4) δ 4.75 (m, 1 H), 4.60 (m, 1 H), 4.10 (q, J = 7 Hz, 1 H), 2.85 (m, 1 H), 1.72 (broad s, 6 H), 1.50 (d, J = 7 Hz, 3 H), 1.09 (s, 3 H), 0.98 (d, J = 7 Hz, 3 H).

Registry No.—**1**, 7641-77-2; **5**, 20379-83-3; **8**, 40265-14-3; **9**, 50590-86-8; **12**, 50590-87-9; **13**, 51751-70-3; **15**, 19835-61-1; **16**, 41694-21-7; triethylamine, 121-44-8; tetracyanoethylene, 670-54-2.

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(12) In cooperation with Drs. W. F. J. Huurdeman. For another synthetic pathway see H. Hogeveen and W. F. J. Huurdeman, *Tetrahedron Lett.*, 1255 (1974).

Double Bond *vs.* Cyclopropane Ring Reactivity toward Different Acids[1]

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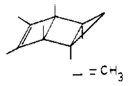
The reactions of compounds **2**, **3**, and **4** with the strong acid $FHSO_3$ and with $HCl-CH_2Cl_2$ have been studied and mechanisms for these reactions are discussed. It is concluded that the reaction with $FHSO_3$ takes place at the methylene groups of the compounds investigated. The reaction with HCl, however, takes place at the cyclopropane rings of compounds **2** and **3** and possibly also of compound **4**. Tentative explanations are given, based on the different nature of the acids and different structural properties of the substrate compounds.

Some aspects of the mechanism of the protonation of cyclopropane, *e.g.*, the relative stability of the face-protonated, edge-protonated, and corner-protonated cyclopropane and the question whether the protonation occurs *via* an inversion or a retention mechanism, have been amply discussed.[2,3] Another aspect of the protonation of cyclopropane, namely the relative reactivity of cyclopropanes and double bonds, has gained less attention. From the few examples known[2d] the general trend seems to be that cyclopropane rings are more reactive toward acids than are carbon–carbon double bonds. We wish to add a new element to this discussion; it appears that in compounds containing a cyclopropane ring as well as a double bond the nature of the acid plays an important role in determining whether the cyclopropane ring or the double bond reacts first. Previously[3a] it was found that compound **1**,



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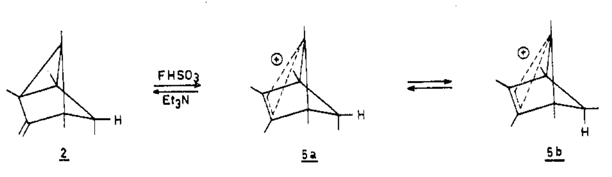
containing a double bond and a cyclopropane ring, reacted at the cyclopropane ring with hydrogen chloride in methylene chloride. Superacids such as $FHSO_3-SO_2ClF$, $FHSO_3-SbF_5$, $FHSO_3-SbF_5-SO_2F_2$, and $HF-BF_3$, however, did not give the product expected upon protonation of the cyclopropane ring. Perhaps reaction at the double bond occurred as the first step under the latter conditions.

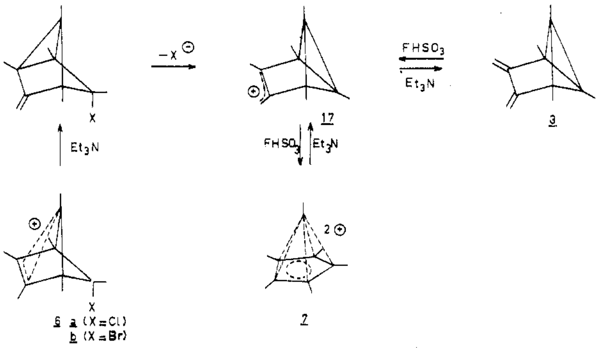
Results and Discussion

The different behavior of the superacids and $HCl-CH_2Cl_2$ toward compounds containing cyclopropane rings and double bonds was investigated with use of the model compounds **2**, **3**, and **4**, containing different numbers of the reactive structural components mentioned. These model compounds are readily accessible in two-step reactions starting from hexamethyl(Dewar benzene).[1,4] In the first step the carbonium ions **5a**, **6**, **7**, and **8**, respectively, are generated and in the second step triethylamine abstracts a proton from these carbonium ions at the methyl group adjacent to the carbon atom bearing the highest positive charge.[4c]

Reactions with $FHSO_3$. The reactions of **2**, **3**, and **4** with $FHSO_3$ show the exact reverse of the triethylamine-induced deprotonation step in the syntheses of **2**, **3**, and **4**. When **2** was dissolved in $FHSO_3$ at −80°, the pmr spectrum of the solution showed the presence of a 3:1 equilibrium mixture[5] of **5a** and its endo-H isomer **5b**. Extraction



of a solution of **3** in methylene chloride with $FHSO_3$ at −90° afforded the dication **7**, which presumably was ob-



tained by successive protonation of the two methylene groups of **3**.[4b] From the literature[6,7] it is known that **4**