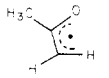
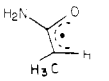
Table IV

| isoxazole | isolated product | $E_a$, kcal/mol | MF HOMO[b] | model MF |
|---|---|---|---|---|
| 3,5-dimethyl-[a] | 2,5-dimethyloxazole | 41.1 | $\alpha + 0.413\beta$ |  |
| 3-amino-5-methyl-[a] | 2-amino-5-methyloxazole | 40.2 | | |
| 5-methyl- | acetylacetonitrile | 41.8 | | |
| 5-amino-3,4-dimethyl-[a] | 3-carbamoyl-2,3-dimethyl-1-azirine | 25.8 | $\alpha + 0.222\beta$ |  |
| 5-amino-4-methyl- | 2-cyanopropionamide | 26.1 | | |

[a] From ref 2b. [b] HMO calculations were carried out by using $h_X$ and $k_{CX}$ parameters from ref 11. The methyl group was calculated as a heteroatom.

When $R_3 \neq H$ and the reaction isoxazole → 1-azirine is exothermic, the 1-azirine is isolated as the major product. When $R_3 \neq H$ and the reaction **5** → **6** is endothermic, the final product is **11**, produced via the nitrile ylide **10**. Finally, when $R_3 = H$ the reaction product is **9**, which can be formed through the ketenimine **8** or directly from **7** via a 1,2 hydrogen shift.

From the experimental results, it seems that the 1,2 hydrogen shift in the nitrene intermediate has a lower energy barrier than the C–C rupture of the 1-azirine to give the nitrile ylide. But, when $R_3 = CH_3$, $NH_2$, the 1,2 shift requires more energy than the C–C rupture of the 1-azirine ring.

For all the studied isoxazoles, according to the kinetic results, the rate-limiting step can be attributed to the 1-azirine formation, and the oxazole and α-carbonylacetonitrile isomers come from the corresponding 1-azirine.

## Experimental Section

Proton nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer and chemical shifts are quoted in δ (parts per million) downfield from tetramethylsilane. Ultraviolet spectra were run on a Beckman Model 24 spectrophotometer. Infrared spectra were obtained on a Beckman IR 8 spectometer. Vapor phase chromatography was performed on a Varian Aerograph Series 2400. Melting points are uncorrected and were determined by the capillary method. Solvents were analytical reagents or otherwise purified by standard methods.

5-Amino-4-methylisoxazole was obtained according to the literature[9] by reaction of 3-aminoisobutyronitrile with $H_2O_2$ in the presence of $Na_2WO_4 \cdot 2H_2O$ as catalyst in methanol. The reaction products were separated by column chromatography on silica gel and sublimation in vacuo.

5-Methylisoxazole was commercially available from Fluka.

Gas-phase reactions were carried out in a Vycor glass reactor (30-cm length and 1.2-cm internal diameter). The reactor was "seasoned" by the thermal decomposition of *n*-butyl bromide at 500 °C. Heating was performed in a Lindberg heavy duty Model 55035 tube furnace. The products were obtained from the trap after reaction tube at the liquid air temperature. In all runs the mass balance between the weight of sample used and the quantitative analysis of the reaction products was higher than 97%.

**5-Amino-4-methylisoxazole.** The products trapped were eluted with water. Compound **2** was removed from the mixture by extraction with chloroform from the aqueous solution. Evaporation in vacuo of the water extract gave **4** as a residue: white crystals (mp 94–96 °C); IR (KBr) 3400, 3200, 2200, 1650, 1300 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) δ 7.6 (br s, 2 H), 3.6 (q, 1 H), 1.2 (d, 3 H).

When **4** was heated under the same conditions as those used for **2**, no reaction was observed and **4** was recovered quantitatively. Hence, an equilibrium must be rejected. This result agrees with the relative thermodynamic stabilities of acetonitrile and the isomeric 1-azirine.[12]

**5-Methylisoxazole.** The trapped products were extracted with chloroform to prevent polymerization of **3**.[10] The removal of **1** from the reaction mixture was impossible due to the polymerization of **3**. For this reason, it was necessary to carry out a reaction to completion to identify **3**, which afforded the following spectral results: IR (KBr) 2900, 2200, 1730, 1650, 1350, 1300 $cm^{-1}$; NMR (chloroform-*d*) δ 2.3 (s, 3 H), 3.4 (s, 2 H); mass spectrum, *m/e* 83 ($M^{+\cdot}$, 10.6), 57 (M – CN, 25.3), 55 (M – $CNH_2$, 16.5), 43 (M – $C_2NH_2$, 100).

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**Registry No.** 1, 5765-44-6; 2, 35143-75-0; 3, 2469-99-0; 4, 71565-78-1.

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# Two-Step Route toward Some [4.3.2]Propellanes and Their Conversion into Stable Tricyclic Cations

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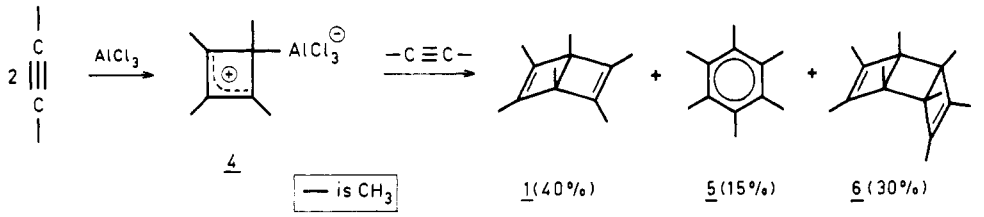
*Received July 31, 1981*

The synthesis of 1,4-tetramethylene(Dewar benzene) (**2**, a [4.2.2]propellane) and its conversion to the [4.3.2]propellanes **3** and **10** are described. Reaction of alcohol **10** with $FSO_3H/SO_2ClF$ at low temperature (–135 °C) yielded tricyclic cation **12**, which rearranged at –75 °C to a mixture of three isomeric cations. The structures and rearrangements of the cations were studied with $^1H$ and $^{13}C$ NMR spectroscopy and deuterium labeling.

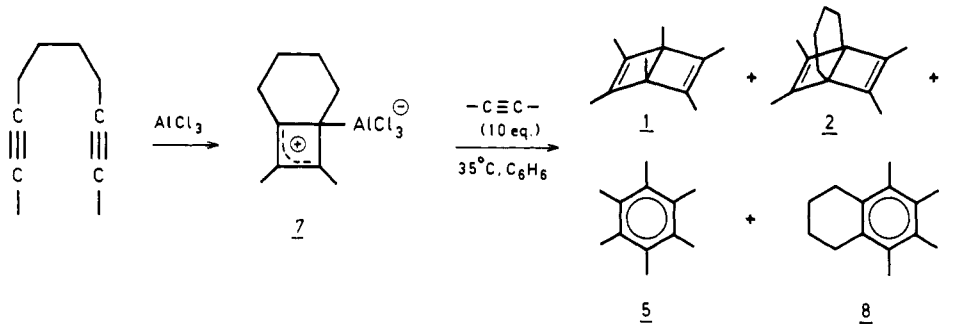
The multifarious chemistry derived from hexamethyl(Dewar benzene) (**1**), as reported by Schäfer and Hellmann,[2] Hogeveen and Kwant,[3] and others formed an impetus for us to develop a synthetic route toward per-

0022-3263/82/1947-0984$01.25/0 

Scheme I




Scheme II




alkylcycloalkano(Dewar benzenes).[4] These compounds were expected to constitute an interesting extension of the "Dewar benzene chemistry" reported so far. In this paper we report the synthesis of the tetramethyl-1,4-tetramethylene(Dewar benzene) (**2**, a [4.2.2]propella-7,9-diene)[5,6] as well as its conversion into the tricyclic ketone **3** (a [4.3.2]propella-7,10-dien-9-one). Furthermore, ketone **3** has been shown to be a suitable substrate for an entry to tricyclic cations, the study of which is related to the recent results of Cargill on photochemical[7] and acid-catalyzed[8] rearrangements of analogous tricyclic ketones as well as to other very recently reported acid-catalyzed rearrangements of [*m.n.*2]propellanes.[9,10]

## Results and Discussion

**Synthesis of Dewar Benzene (2).** The synthesis of hexamethyl(Dewar benzene) (**1**) involves an $AlCl_3$-catalyzed trimerization of 2-butyne at 35 °C in benzene.[2] This reaction supposedly proceeds via the $AlCl_3$ $\sigma$ complex **4**, which reacts with 2-butyne to give **1**. Subsequently, it was found that **1** can be obtained also if **4** in $CH_2Cl_2$ is decomposed by $Me_2SO$ at 17–35 °C in the presence of 2-butyne, compounds **5** and **6** being the other reaction products (Scheme I).[11] When a reaction of the $AlCl_3$ $\sigma$ complex **7**, prepared from 2,8-decadiyne and $AlCl_3$,[12] was performed with 2-butyne, Dewar benzene (**2**) was obtained as one of the reaction products (Scheme II) in yields varying from 15% to 22%. A necessary condition was the use of benzene as the solvent.[13] After a solution of 2-butyne (10 equiv) in benzene was added to a homogeneous solution of **7** in benzene at 5 °C, a two-layer system was formed, the upper layer containing 2-butyne and the lower layer complex **7** and a small quantity of 2-butyne. The exothermic cycloaddition occurred at about 35 °C, and the products **1** and **2** (and isomeric Dewar benzenes) were taken up in the upper layer, whereas in the lower layer **7** was gradually replaced by **4**.[15] The reaction is presented schematically in Figure 1; it shows the necessity of using a large excess (10 equiv) of 2-butyne in the reaction. The reaction was stopped after 1.5 h at 35 °C, although **7** and 2-butyne were still present in the lower and upper layer, respectively. Complex **4**, however, strongly prevailed in the lower layer, and a prolonged reaction time would

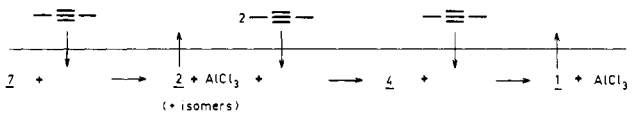
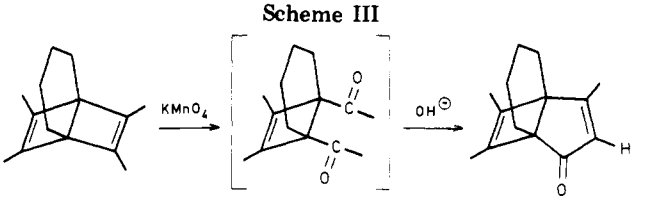



**Figure 1.** Schematic presentation of the reaction between complex **7** and 2-butyne in a two-phase system.

Scheme III




(1) To whom correspondence should be addressed.
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(6) (a) Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 349. (b) Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1974**, 2813. (c) Weinges, K.; Klessing, K. *Chem. Ber.* **1974**, *107*, 1915. (d) Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 4499.
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(11) Hogeveen, H.; Jorritsma, H.; Wade, P. A.; van Rantwijk, F.; Koster, P. B.; Prooi, J. J.; Sinnema, A.; van Bekkum, H. *Tetrahedron Lett.* **1974**, 3915.
(12) Driessen, P. B. J.; Hogeveen, H. *J. Am. Chem. Soc.* **1978**, *100*, 1193.
(13) Normally, the $AlCl_3$ $\sigma$ complexes of cyclobutadienes[4,14] are prepared and used in $CH_2Cl_2$ solution.
(14) Kok, D. M. Ph.D. Thesis, The University of Groningen, 1981.
(15) Decomposition products were formed also, but these were present in the lower layer only. The amounts of benzene derivatives **5** and **8** present in the upper layer increased during the course of the reaction.

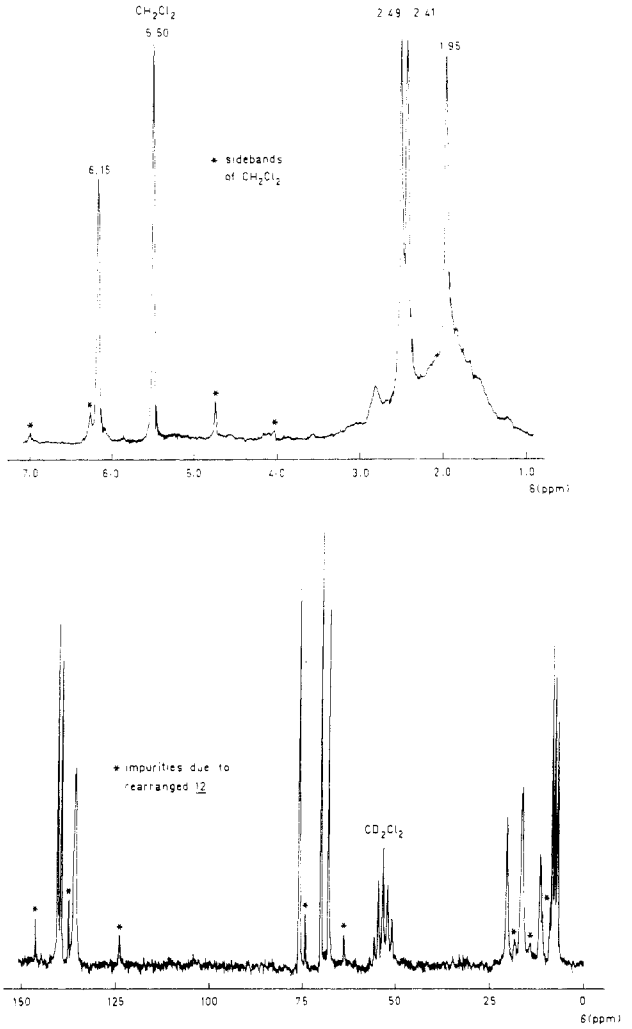



**Figure 2.** $^1H$ (top) and $^{13}C$ (bottom) NMR spectra of the solution obtained from alcohol **10** in $FSO_3H/SO_2ClF$ at −86 and −105 °C, respectively.

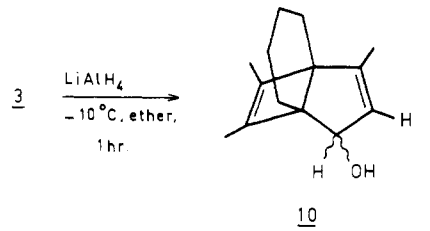
mainly result in addition of 2-butyne to complex **4**, affording **1**. Moreover, **2** slowly decomposed under the reaction conditions.

If **7** was allowed to react with an excess of 2-butyne at 35 °C with $CH_2Cl_2$ as the solvent[13] (giving a homogeneous solution) **8** but not **2** (or isomeric Dewar benzenes) could be detected in the reaction mixture. Presumably, the point of using benzene as the solvent is that the reaction products (Dewar benzenes) were transferred to the upper layer, in which they were protected quite effectively against aromatization and/or decomposition by action of $AlCl_3$, which was mainly present in the lower layer. An additional advantage in using benzene as the solvent is that the upper layer contained (Dewar) benzene derivatives only, whereas the decomposition products and the remaining complexes **4** and **7** were present in the lower layer. By disposal of this layer the workup procedure was facilitated substantially.

**Synthesis of Propellanes 3 and 10.** Dewar benzene **2** was an attractive starting material for the synthesis of precursors for tricyclic cations related to the bicyclo[3.2.0]- and -[2.2.1]heptadienyl cations, which we investigated recently.[16]

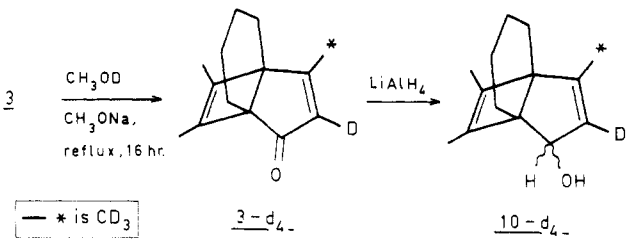
Alkaline oxidation of **2** with $KMnO_4$ afforded in 64% yield the tricyclic ketone **3** (Scheme III). Analogously to

Scheme IV



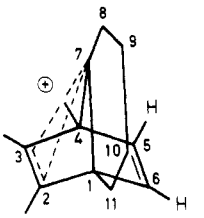

**10**

Scheme V




**3**-$d_4$ **10**-$d_4$

Table I. $^1H$ and $^{13}C$ NMR Chemical Shifts of Cation **12**




**12**

| | |
|---|---|
| $^1H$ NMR[a,c] | δ 6.15 (C-5,6 hydrogens), 2.49 and 2.41 (C-2,3 methyls), 1.95 (C-4 methyl), 2.9–1.2 (C-1,7 tetramethylene) |
| $^{13}C$ NMR[b,c] | δ 134.9 and 134.2 (C-2,3), 130.8 and 130.6 (C-5,6, d, $J$ = 180 Hz), 74.9,[d] 69.4, and 67.6 (C-1,4,7), 23.0, 19.4, 19.1, and 14.7[e] (C-8,9,10,11, t, $J$ = 130 Hz), 11.7, 11.2, and 10.6 (C-2,3,4 methyls, q, $J$ = 130 Hz) |

[a] Measured in δ units relative to internal $CH_2Cl_2$ at δ 5.50. [b] Measured in δ units relative to internal $CD_2Cl_2$ at 53.8. [c] All chemical shifts are calculated relative to external $Me_4Si$ as a 10% solution in $CD_3COCl$ at δ 0.00. [d] This signal is tentatively assigned to C-7. [e] This signal is tentatively assigned to C-8, because in analogous cations the C-7 methyl also absorbs at relatively high-field (δ 4 ± 2).[16a]

the oxidation of **1**,[17] the intermediately formed diacetyl derivative **9** underwent an intramolecular aldol condensation, affording **3**. Reduction of **3** with $LiAlH_4$ yielded alcohol **10** (95%, Scheme IV) as a ca. 3:1 mixture of the two diastereomers[18] (see Experimental Section). For a tracer study the deuterium labeled alcohol **10**-$d_4$ was prepared as shown in Scheme V.

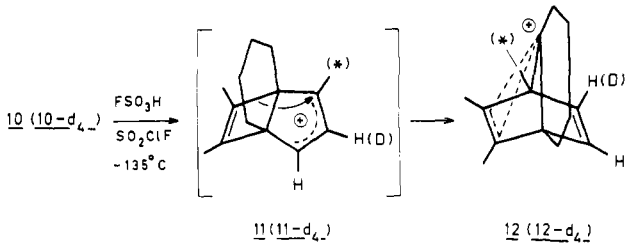
**Formation of Tricyclic Cation 12 and Its Rearrangement.** When alcohol **10** was dissolved in $FSO_3H/SO_2ClF$ at −135 °C a light yellow solution was obtained, the $^1H$ and $^{13}C$ NMR spectra of which are presented in Figure 2. On the basis of these spectral data (summarized in Table I) and literature data of analogous cationic systems,[16a] we propose cation **12**[19] to be present. This species

(16) (a) Hogeveen, H.; van Kruchten, E. M. G. A. *Top. Curr. Chem.* **1979**, *80*, 89. (b) Carnadi, H.; Giordano, C.; Heldeweg, R. F.; Hogeveen, H.; van Kruchten, E. M. G. A. *Isr. J. Chem.* **1981**, in press. (c) Hogeveen, H.; van Kruchten, E. M. G. A., accepted for publication in *J. Org. Chem.*

(17) Junker, H.-N.; Schäfer, W.; Niedenbrück, H. *Chem. Ber.* **1967**, *100*, 2508.

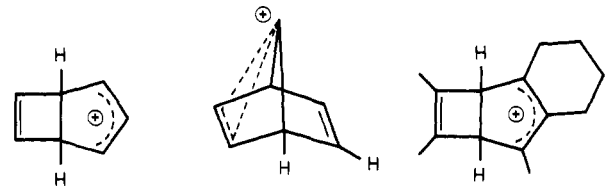
(18) No attempt has been made to assign which of the isomers is the major one. The endo and exo alcohol afford the same cation on reaction with superacid.

Scheme VI




was formed by a 1,2 Wagner–Meerwein shift in the initially generated, but not observed, cation **11**. Analogously, treatment of the labeled alcohol **10**-$d_4$ with $FSO_3H/SO_2ClF$ afforded cation **12**-$d_4$ via intermediate **11**-$d_4$ (Scheme VI). The $^1H$ NMR spectrum of **12**-$d_4$ differed from that of **12** by a reduced intensity of the signal at $\delta$ 6.15 (due to the C-5,6 hydrogens) as well as by the absence of the signal at $\delta$ 1.95 (due to the bridgehead methyl group).

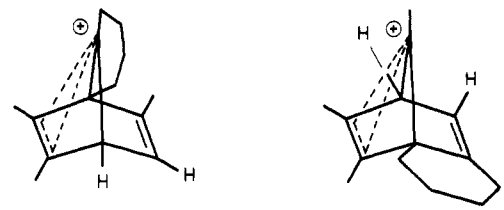
Above −75 °C cation **12** rearranged irreversibly to a mixture of three isomeric cations A and B (2x). The number of isomers is based on the proton-noise-decoupled $^{13}C$ NMR spectrum (see data in Table II), which clearly shows the presence of 21 skeletal carbon atoms (the tetramethylene chain being considered as a substituent and omitted in the structures) belonging to one [3.2.0] isomer (characteristic[16a] allylic absorptions at $\delta$ 234.8, 233.3, and 156.7) and two [2.2.1] isomers. In addition, in the region $\delta$ 6–36 are found 17 of the expected 21 peaks, which originate from the methyl and methylene carbon atoms (it is reasonable to assume that in this mixture of structurally closely related cations some peaks coincide). Further information is obtained from the proton-coupled $^{13}C$ NMR spectrum, showing six doublets for skeletal carbon atoms (two $sp^2$ carbon atoms at $\delta$ 124.3 and 118.9 and four $sp^3$ carbon atoms at $\delta$ 68.2, 66.4, 62.7, and 56.7). On the basis of these data the mixture is proposed to consist of one [3.2.0] isomer, A, and of two [2.2.1] isomers, B. Strong




A B (2x) 13

indication that the tetramethylene chain in A is situated as shown in structure **13** is formed by the triplet found at $\delta$ 36.0 in the $^{13}C$ NMR spectrum. Such a relatively low-field signal[20] is characteristic for a terminal allylic alkyl substituent (compare, e.g., the absorptions of terminal allylic methyl groups at $\delta$ 22 ± 3 with those of methyl groups at other positions in both [3.2.0] and [2.2.1] isomers at $\delta$ 12 ± 3[16a]).[21]

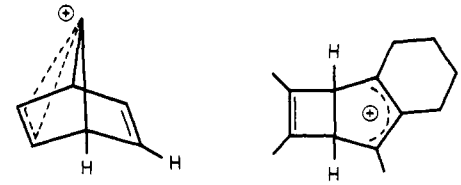
Due to the complexity of both the $^{13}C$ NMR spectra and (especially) the $^1H$ NMR spectra of the mixtures of cations, which originate from cation **12** or cation **12**-$d_4$, more definite structural assignments for B are hampered. On the basis of the results of the bicyclo[3.2.0]heptadienyl cations studied previously,[16a] the structures of the two remaining cations of type B might very well be **14** and **15**; however, unambiguous evidence for this proposal has not been obtained.




14 15

In conclusion, the data discussed in this paper show that the tricyclic ketone **3** is a valuable entry into this class of tricyclic cations, but more experiments (synthesis of precursors with a different substitution pattern and NMR spectroscopic analysis of stable cation solutions) are necessary to study the chemical behavior of these tricyclic cations in more detail.

Table II. $^1H$ and $^{13}C$ NMR Chemical Shifts[a] of the Mixture of Cations 13 and B at −50 °C




B (2x) 13

| | |
|---|---|
| $^{13}C$ NMR | skeletal carbon atoms: allylic part of **13** at 234.8, 233.3, and 156.7; $sp^2$ carbons of **13** and B (2x) at 141.5, 140.0, 139.5, 138.8, 135.7, 134.3, 132.9, 131.3, 124.3 (d, $J$ = 165 Hz), and 118.9 (d, $J$ = 175 Hz); $sp^3$ carbons of **13** and B (2x) at 74.0, 73.1, 70.6, 68.2 (d, $J$ = 155 Hz), 66.4 (s), 66.4 (d, $J$ = 155 Hz), 62.7 (d, $J$ = 155 Hz), and 56.7 (d, $J$ = 155 Hz) |
| | methylene carbon atoms (t, $J$ = 130 Hz), at 36.0, 30.2, and 26.6 |
| | methyl carbon atoms (q, $J$ = 130 Hz) at 12.9, 11.9, 11.6, 8.2, and 6.1 |
| | methyl or methylene carbons at 24.1, 23.9, 23.1, 22.4, 21.5, 20.3, 20.1, 19.8, and 15.7 |
| $^1H$ NMR | methyl signals at $\delta$ 3.06 (br), 2.47, 2.41, 2.16, 1.93, 1.90, and 1.76 methylene signals between $\delta$ 2.9 and 1.2 (broad peaks under the methyl peaks) |
| | hydrogen signals (br) at 6.04, 5.86 (vinylic), 4.78, 4.54, 3.93 and 3.84 [the latter two peaks are tentatively assigned to an AB quartet at 3.99 and 3.78 ($J \approx$ 13 Hz) of cation **13**] |

[a] See footnotes *a–c* in Table I.

## Experimental Section

**General Remarks.** Melting points were determined on a Mettler FP-2 melting point apparatus equipped with a microscope. The IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on an AEI MS-902 by Mr. A. Kiewiet. UV spectra were recorded on a Beckman DB-G spectrophotometer. Elemental microanalyses were performed in the analytical section of our department by Mr. J. Ebels. $^1H$ NMR spectra of the neutral compounds were recorded at 60 or 200 MHz with a Hitachi Perkin-Elmer R-24B or a Nicolet NT 200 spectrometer, respectively. Natural-abundance $^{13}C$ NMR spectra of the neutral compounds were obtained with a Varian XL-100 or

(19) In structure **12** the hydrogens at the "unbound" double bond (C-5,6) are different but by circumstance absorb at the same $^1H$ NMR chemical shift ($\delta$ 6.15). However, the intrinsic difference of these positions is reflected in the $^{13}C$ NMR spectrum, in which doublets are found at $\delta$ 130.6 and 130.8.

(20) In general, the carbon atoms of such a methylene chain absorb at $\delta$ 23 ± 5 (see Experimental Section and Table I).

(21) Unfortunately, due to the complexity of the spectrum, it was impossible to assign the multiplicities (triplet or quartet) of the $^{13}C$ NMR peaks between $\delta$ 15.7 and 24.1, in which region, among others,[20] the terminal allylic methyl groups are found.[16a]

a Nicolet NT 200 operating at 25.16 and 50.31 MHz, respectively, with the aid of Fourier transform. The spectra on the Nicolet NT 200 were recorded by Drs. K. S. Fongers. Chemicals shifts for the $^1H$ and $^{13}C$ NMR spectra are reported in parts per million relative to internal $Me_4Si$ at $\delta$ 0.00. The NMR spectra of the cations were recorded on JEOL C 60-HL ($^1H$ NMR; 60 MHz) and Varian XL-100 ($^{13}C$ NMR; 25.16 MHz) spectrometers, both equipped with a variable-temperature probe. Chemical shifts of the cations are denoted in parts per millon relative to external $Me_4Si$ as a 10% solution in $CD_3COCl$ at $\delta$ 0.00. The solvents were purified by common methods, and $AlCl_3$ was sublimed twice before use. 2-Butyne, 2,8-decadiyne, $FSO_3H$, and $SO_2ClF$ were commercially available products and were used without further purification.

**7,8,9,10-Tetramethyltricyclo[4.2.2.0$^{1,6}$]undeca-7,9-diene (2).** Under an atmosphere of dry nitrogen a solution of 2.68 g (20 mmol) of 2,8-decadiyne in benzene (20 mL) was added dropwise to a mechanically stirred suspension of 2.8 g (21 mmol) of $AlCl_3$ in benzene (20 mL) at 5 °C. The solution was warmed to room temperature and stirred for an additional 0.5 h. The homogeneous solution was cooled (0 °C), and a solution of 10.8 g (200 mmol) of 2-butyne in benzene (10 mL) was added dropwise, after which two layers formed. The solution was kept at 35 °C (water bath) and stirred for 1.5 h. It was cooled to 10 °C, the upper layer was decanted, and the remaining lower layer was treated twice with benzene (10 mL) with stirring for 5 min. To the combined "upper layers" was added a solution of $Me_2SO$ (20%) in benzene until the reddish color had vanished. The solution was washed twice with water (20 mL) and dried ($Na_2SO_4$), and the solvent was removed by using a rotatory evaporator. Part of the hexamethylbenzene (**5**) was removed from the crude reaction mixture by several treatments with *n*-pentane (5–10 mL), in which **5** is poorly soluble. The solvent and hexamethyl(Dewar benzene) were removed in vacuo from the reaction mixture [20 °C (0.01 mmHg)], and the residue was dissolved in *n*-pentane and subsequently stored at −40 °C during one night, after which the precipitated hexamethylbenzene was removed by filtration. After evaporation of the *n*-pentane, the resulting mixture was kept under $N_2$ at 120 °C for 2 h, in order to aromatize the Dewar benzenes isomeric with **2**. Distillation with a short Vigreux column provided the product **2** in yields varying from 15% to 22% (0.55–0.82 g, 3.0–4.4 mmol): bp 40 °C (0.001 mmHg); mp ca. 24 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.9–1.7 (br, C-2,3,4,5 hydrogens), 1.59 (C-7,8,9,10 methyls); $^{13}C$ NMR ($CDCl_3$) $\delta$ 11.4 (C-7,8,9,10 methyls), q, $J$ = 125 Hz), 21.5 and 23.3 (C-2,5 and C-3,4, t, $J$ = 125 Hz), 51.8 (C-1,6), 144.3 (C-7,8,9,10); mass spectrum, $m/e$ 188 ($M^+$). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.24; H, 10.88. The residue of the distillation contained **8** ($^1H$ NMR: methyl resonances at $\delta$ 2.10 and 2.18[22]) together with **5** and decomposition products. Variations in reaction time (0.5–3.5 h), reaction temperature (0–55 °C), and/or the amount of 2-butyne (2–15 equiv) did not improve the yield of **2**.

**7,10,11-Trimethyltricyclo[4.3.2.0$^{1,6}$]undeca-7,10-dien-9-one (3).** A cooled (0 °C) solution of 1185 mg (7.5 mmol) of $KMnO_4$ and 250 mg (6.25 mmol) of NaOH in 40 mL of $H_2O$ was added dropwise with mechanical stirring to a cold (−10 °C) solution of 940 mg (5 mmol) of **2** in 50 mL of *t*-BuOH, 10 mL of $H_2O$, and 25 g of ice. During the addition the temperature was kept below 0 °C, and stirring was continued for 1 h. $MnO_2$ was filtered with suction (using Celite) and washed with ether. The resulting filtrate was distilled to give ether (34 °C) and the azeotropic mixtures $H_2O$/*t*-BuOH (79 °C) and **3**/$H_2O$ (99–100 °C) (**3** crystallized partly in the cooler). The aqueous layer, containing ketone **3**, was extracted with ether (3 × 20 mL), the combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo to yield 648 mg (3.21 mmol, 64%) of **3**. Analytically pure **3** was obtained as a white crystalline material in 52% yield (520 mg, 2.57 mmol) by crystallization from *n*-pentane (−30 °C): mp 61.5–62 °C; IR (Nujol) 1695 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.57–1.60 (C-10,11 methyls), 1.2–2.0 (br, C-2,3,4,5 hydrogens), 2.00 (C-7 methyl, d, $J$ = 1.8 Hz), 5.61 (C-8 hydrogen, $q$, $J$ = 1.8 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.6, 10.5, 16.3 (C-7,10,11 methyls, $q$, $J$ = 125 Hz), 19.3, 19.5, 23.7, and 24.7 (C-2,3,4,5, t, $J$ = 125 Hz), 57.8 and 58.9 (C-1,6), 127.5 (C-8, d, $J$ = 170 Hz), 140.9 and 143.9 (C-10,11), 180.2 (C-7), 209.8 (C-9); exact mass for $M^+$ calcd $m/e$ 202.136, found $m/e$ 202.137. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.93; H, 9.03.

**10,11-Dimethyl-7-(trideuteriomethyl)-8-deuteriotricyclo[4.3.2.0$^{1,6}$]undeca-7,10-dien-9-one (3-$d_4$).** A solution containing 100 mg of ketone **3** and 25 mg of $CH_3ONa$ in 5 mL of $CH_3OD$ was kept at reflux overnight. The methanol was evaporated under reduced pressure, and the solid residue was treated with water and extracted with $CH_2Cl_2$. The organic layer was washed with water until neutral and dried over $MgSO_4$, and the solvent was removed in vacuo by using a rotatory evaporator, giving a nearly quantitative yield of **3-$d_4$**: 95 mg (95%); the $^1H$ NMR spectrum differed from that of **3** by lacking the signals at $\delta$ 5.61 (due to the hydrogen at C-8) and 2.00 (due to the C-7 methyl); mass spectrum, $m/e$ 206 ($M^+$).

**7,10,11-Trimethyltricyclic[4.3.2.0$^{1,6}$]undeca-7,10-dien-9-ol (10).** An excess of $LiAlH_4$ (ca. 300 mg, 9 mmol) was added to a cooled (−12 °C) solution of 303 mg (1.5 mmol) of **3** in 30 mL of anhydrous ether. After being stirred for 1 h, the reaction mixture was warmed to room temperature, and stirring was continued 15 min. The excess of $LiAlH_4$ was quenched at 0 °C by the simultaneous dropwise addition of a 20% aqueous $NH_4Cl$ and a 20% aqueous NaOH solution. The resulting reaction mixture was filtered and extracted with ether (3 × 20 mL). The combined organic layers were washed twice with $H_2O$ (25 mL), dried over $MgSO_4$, and filtered, and the solvent was evaporated to yield 290 mg (1.42 mmol, 95%) of a ca. 3:1 mixture of the diastereomeric alcohols **10**:[18] IR (neat) 3350 cm$^{-1}$ (br); $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 5.31 and 5.21 (ca. 1:3, C-8 hydrogen), 4.45 and 4.35 (ca. 1:3, C-9 hydrogen), 1.72 (C-7 methyl), 1.66 (C-10,11 methyls), 1.20–1.90 (br, C-2,3,4,5 hydrogens); $^{13}C$ NMR ($CDCl_3$, 50.31 MHz) for minor isomer[18] $\delta$ 8.8, 10.7, and 14.3 (C-7,10,11 methyls, q, $J$ = 125 Hz), 18.5, 19.9, 21.6, 24.7 (C-2,3,4,5, t, $J$ = 125 Hz), 55.5 and 60.8 (C-1,6), 75.9 (C-9, d, $J$ = 150 Hz), 125.7 (C-8, d, $J$ = 155 Hz), 140.8, 149.9, and 152.8 (C-7,10,11); major isomer[18] $\delta$ 10.8, 12.4, and 14.2 (C-7,10,11 methyls, q, $J$ = 125 Hz), 18.0, 18.1, 23.7, and 27.7 (C-2,3,4,5, t, $J$ = 125 Hz), 54.6 and 59.5 (C-1,6), 81.2 (C-9, d, $J$ = 150 Hz), 126.2 (C-8, d, $J$ = 155 Hz), 138.5, 147.6, and 149.9 (C-7,10,11); exact mass for $M^+$ calcd $m/e$ 204.151, found $m/e$ 204.149. This mixture was used as such for the cation preparations.

**10,11-Dimethyl-7-(trideuteriomethyl)-8-deuteriotricyclo[4.3.2.0$^{1,6}$]undeca-7,10-dien-9-ol (10-$d_4$).** The reaction of $LiAlH_4$ with **3-$d_4$** (75 mg, 0.36 mmol) was carried out as described above for the reduction of **3** to yield 65 mg (0.31 mmol, 87%) of alcohol **10-$d_4$**. The $^1H$ NMR spectrum of **10-$d_4$** differed from that of **10** by lacking the hydrogen signals at $\delta$ 5.31 and 5.21 (due to the hydrogen at C-8) and the allylic methyl signal at $\delta$ 1.72 (due to the C-7 methyl); mass spectrum, $m/e$ 208 ($M^+$).

**Generation of Cations in Strongly Acidic Media.**[23] In a typical experiment ca. 80 mg of $FSO_3H$ was introduced into a dry, clean $^1H$ NMR tube, followed by condensation of $SO_2ClF$ (~0.35 mL) at −135 °C. With the aid of a cooled glass rod ca. 30 mg of precursor was introduced and the resultant mixture homogenized. For the $^{13}C$ NMR spectra appropriately larger amounts were used. Immediately after the generation of the cations, the samples were inserted into the precooled NMR probe. The temperatures at which the spectra were recorded were measured with a copper–constantan thermocouple.

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**Registry No.** **2**, 80228-46-2; **3**, 80228-47-3; **3-$d_4$**, 80228-48-4; **10** (isomer 1), 80228-49-5; **10** (isomer 2), 80286-99-3; **10-$d_4$**, 80228-50-8; **12**, 80293-81-8; **12-$d_4$**, 80293-79-4; **13**, 80227-62-9; **14**, 80293-82-9; **15**, 80293-80-7; 2,8-decadiyne, 4116-93-2; 2-butyne, 503-17-3.

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