Notes

Identification of 1- and 10-Methylperhydrotriquinacene in Tricycloundecane Rearrangement Products

Yoshiaki Inamoto,* Koji Aigami, Yoshiaki Fujikura, Naotake Takaishi, and Kiyoshi Tsuchihashi

Tochigi Research Laboratories, Kao Soap Company, Ltd., 2606 Akabane, Ichikaimachi, Tochigi 321-34, Japan

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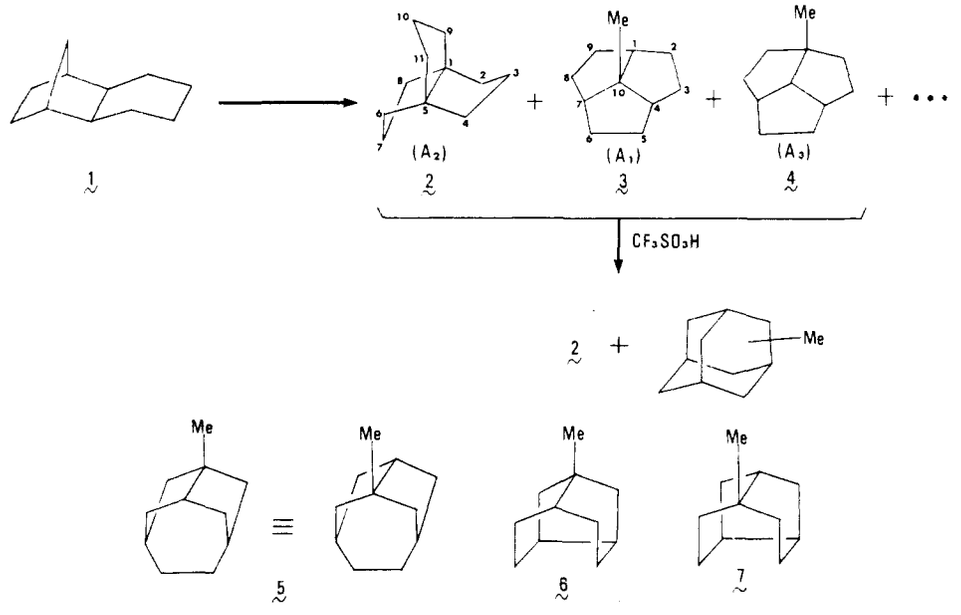
Trifluoromethanesulfonic acid catalyzed skeletal rearrangement of *exo-cis*-2,3-tetramethylenenorbornane (tricyclo[6.2.1.$0^{2,7}$]undecane (**1**)) has been shown to afford a complex mixture of products.[1] Sixteen compounds were recognized in this mixture upon examination on Golay column GC–MS, while conventional VPC separated them into eight fractions. The first-eluted fraction (fraction A) consisted of three compounds denoted as unknowns A_1, A_2, and A_3. We assigned on ^{13}C NMR spectroscopic evidences the structure of [3.3.3]propellane (tricyclo[3.3.3.$0^{1,5}$]undecane (**2**)) to A_2 and 7- and 1-methylisotwistane (7- and 1-methyltricyclo[4.3.1.$0^{3,7}$]decane) to A_1 and A_3, respectively. In connection with our progressing study on "local" pathways of the tricycloundecane rearrangement, isomerization of fraction A was examined. Preliminary experiments showed that unknown A_1 and A_3 were transformed relatively fast into 1- and 2-methyladamantane, whereas A_2 (**2**) rearranged rather sluggishly. This fact made possible the isolation of the propellane **2** from fraction A. The propellane thus isolated showed a different ^{13}C NMR spectrum from that described in the previous report.[1] The result necessarily led us to find the methylisotwistane structures for A_1 and A_3 to be in error. Now the correct methylperhydrotriquinacene structures (**3** and **4**) are assigned to them and these structure determinations are established by an independent synthesis.

Isomerization of a sample of fraction A, consisting of 34.3% A_1, 18.7% A_2 (**2**), and 47.0% A_3, for 16 h in the presence of 4 molar equiv of trifluoromethanesulfonic acid in methylene chloride as solvent at reflux gave a mixture comprising 18.5% **2**, 33.2% 1-methyladamantane, 44.8% 2-methyladamantane, 0.5 and 2.2% unreacted A_1 and A_3, respectively, and 0.8% of an unknown compound. The propellane was thus quite unreactive under these reaction conditions.[2] The reaction mixture was fractionated on a preparative VPC to afford the first-eluted fraction containing 85.6% **2**, 1.9% A_1, and 8.5% A_3. Slow sublimation gave a sample of **2** with 94% purity in 0.97% yield based on **1**. Its ^{13}C NMR chemical shifts (Table I) and three major peaks of the mass spectrum were in good agreement with those[3] (δ_C 24.61, 40.33, 60.38, and *m/e* 150, 107, 79) of an authentic specimen prepared by Alder. In turn, the three ^{13}C NMR signals are consistent with the structure of C_{3h} symmetry (**2**) determined by an empirical force field calculation.[4] This characteristic molecular structure is also reflected in its mass spectrum, only three major peaks being found, as referred to above. The present isolation offers a convenient method of preparing [3.3.3]propellane which otherwise would be obtainable only via elaborate synthetic routes.[5]

Samples of fraction A were eluted through the preparative VPC column, and the former one-third portions of the peaks were collected. The fractions collected in this way were again fractionated, in the same way, to effect further concentration of A_1. The combined fractions thus obtained comprised 86.8% A_1, 10.0% **2**, and 3.2% A_3. This mixture gave a ^{13}C NMR spectrum consisting of six signals. Two of them (δ_C 24.57 (t) and 40.32 (t)) with low relative intensities agreed with those of **2**. The third signal of **2** (δ_C 60.33 (s)), arising from the quaternary carbon atoms, was too weak to be detected. It also seems probable to believe that all the signals of A_3 were hidden in the background noise because of low concentration. The remaining four signals for the mixture (δ_C 28.25 (q, 1), 31.50 (t, 6), 52.66 (d, 3), and 62.15 (s, 0.4)) should belong to A_1. The molecule of A_1 is thus appreciably symmetrical, having a methyl and a quaternary carbon atom. The same mixture gave a ^1H NMR spectrum in which was observed a distinct, sharp singlet (δ_H 1.08) for the methyl protons in the background of broad, complex multiplet (δ_H 1.0–2.2). This indicated that the methyl group was one of the substituents on the quaternary carbon atom. Careful examination of all the possible bridge-



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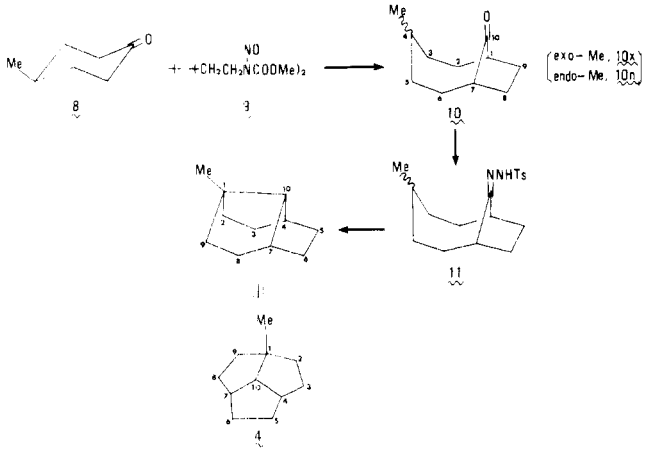
head methyl derivatives of 19 reasonably stable tricyclodecanes[4,6] showed that 10-methylperhydrotriquinacene (10-methyltricyclo[5.2.1.$0^{4,10}$]decane (**3**)) was the only possible structure corresponding to the ^{13}C and the ^{1}H NMR spectra. It has been found previously[1] that A_1 was inert toward bromination under the conditions under which methyladamantanes, homoadamantane, and 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane) were highly reactive. A perhydrotriquinacene structure for A_1 is consistent with this result, in view of the relative stabilities of bridgehead cations of bicyclo[3.3.0]octane, bicyclo[3.3.1]nonane, adamantane, and homoadamantane, as evidenced from the solvolysis rates of their arenesulfonates and halides.[7] Assignment of the ^{13}C NMR signals of 10-methylperhydrotriquinacene (**3**) as shown on Table I could be done unequivocally only on the basis of its molecular structure with C_{3v} symmetry.

Fraction A gave 13 ^{13}C NMR signals.[1] Subtraction of the three for the propellane **2** and the four for 10-methylperhydrotriquinacene (**3**) left six to be allotted to A_3: δ_C 27.65 (q, 1), 31.58 (t, 4), 39.31 (t, 2), 45.35 (d, 2), 51.36 (s, 0.4), 61.66 (d, 1). ^{1}H NMR spectrum of the fraction contained two sharp singlets at δ_H 1.05 and 1.08. Since the latter signal arose from A_1 as stated above, the former should belong to A_3. These NMR spectra indicated that A_3 also has a methyl substituted on a bridgehead. However, no bridgehead-methylated tricyclodecane[6] exists that satisfies the molecular symmetry and structural features required by the NMR spectra. The intensity of the triplet carbon signal at δ_C 31.58 was quite large when compared to those of other signals. This made us suspect that the signal might arise from two different kinds of carbon atoms which had coincidentally the same chemical shifts. Then, by assuming seven kinds of carbon atoms, four structures (**4–7**) with C_s symmetry are consistent with the spectra. Similarity in the mass spectra of A_1 and A_3[1] strongly suggested the same skeletal structure for both compounds. 1-Methylperhydrotriquinacene (**4**), therefore, would be the best candidate for A_3. Instability of the tricyclodecane skeletons of **5–7**[6b] also seems contradictory to the relatively slow isomerization, and hence the relatively high stability, of A_3. In order to establish the structure **4** for A_3, an independent synthesis of **4** was made via the unambiguous route shown below.



Reaction[8] of 4-methylcyclohexanone (**8**) with the dicarbene generated from dimethyl *N,N'*-dinitroso-*N,N'*-tetramethylenedicarbamate (**9**)[9] gave 4-methylbicyclo[5.2.1]decan-10-one (**10**).[10] Golay GC–MS showed **10** to be an ca. 6:4 mixture of the two isomeric ketones **10x** and **10n**.[10] The ketone mixture **10** was converted to the corresponding tosylhydrazone (**11**) in the usual manner,[8] and the sodium salt of **11** was pyrolyzed[8] to give 1-methylperhydrotriquinacene (**4**). The ^{13}C NMR spectrum of **4** thus synthesized was in complete agreement with that of A_3 described above. The VPC retention times and the mass spectra of both compounds, as measured on the Golay GC–MS, were also identical.

Table I. ^{13}C NMR Chemical Shifts of [3.3.3]Propellane (2) and 10- and 1-Methylperhydrotriquinacene (3 and 4)

compound	registry no.	^{13}C NMR chemical shifts, δ_C (multiplicity, rel intensity; assignment)
2	51027-89-5	24.57 (t, 3; C-3, −7, −10), 40.32 (t, 6; C02, −4, −6, −8, −9, −11), 60.33 (s, 0.8; C-1, −5)
3	64822-64-6	28.25 (q, 1; methyl), 31.50 (t, 6; C-2, −3, −5, −6, −8, −9), 52.66 (d, 3; C-1, −4, −7), 62.15 (s, 0.4; C-10)
4	64822-63-5	27.65 (q, 1; methyl), 31.58 (t, 4; C-3, −5, −6, −8), 39.31 (t, 2; C-2, −9), 45.35 (d, 2; C-4, −7), 51.36 (s, 0.4; C-1), 61.66 (d, 1; C-10)

Assignment of the two triplets (δ_C 31.58 and 39.31) in the ^{13}C NMR spectrum of 1-methylperhydrotriquinacene (**4**) may be made by reference to the effects of methyl substitution on the chemical shifts for *cis*-bicyclo[3.3.0]octane.[11] Introduction of an *endo*-2-methyl into the bicyclooctane caused chemical shift changes by +4.7 ppm (downfield) on C-1 bridgehead, +6.8 on C-3, −1.8 on C-4, and +1.5 on C-6 and C-7, but no effect on the C-5 bridgehead. By combination of these increments with the chemical shifts for 1-methyl-*cis*-bicyclo[3.3.0]octane under an assumption of simple additivity and with an approximation of the effect of methylene by that of methyl,[12] the chemical shifts of C-2 and C-3 in **4** are calculated to be δ_C 41.6 (= 41.9 − 1.8 + 1.5) and 34.2 (= 25.9 + 6.8 + 1.5), respectively. Then, it seems reasonable to assign the experimental quadruple-intensity signal at δ_C 31.58 to C-3 (and C-8) and the double-intensity one at δ_C 39.31 to C-2 (and C-9). The δ_C 31.58 signal also should be assigned necessarily to C-5 and C-6 on consideration of signal intensity.

Similar treatment for C-1 and C-10 birdgeheads of 1-methylperhydrotriquinacene (**4**) gave the calculated δ_C 49.8 (= 49.8 + (2 × 0.0)) and 60.3 (= 50.9 + 2 × 4.7)), respectively, thus reproducing well the experimental signals, δ_C 51.36 and 61.66. The same procedures were applied to 10-methylperhydrotriquinacene (**3**) to give the chemical shifts: δ_C 50.9 (=50.9 + (2 × 0.0)) for C-1, 34.2 (=25.9 + 6.8 + 1.5, or =34.5 − 1.8 + 1.5) for C-2, and 59.2 (=49.8 + (2 × 4.7)) for C-10. These figures are in fair agreement with the corresponding experimental chemical shifts: δ_C 52.66 for C-1, 31.50 for C-2, and 62.15 for C-10. The result is considered to render additional support to the structure determination of A_1.

According to a prediction of the rearrangement pathways on the basis of calculated thermodynamic stabilities of possible tricycloundecane and methyltricyclodecane isomers,[4] methylperhydrotriquinancenes were considered to be one of the most important intermediates in methyl extrusion processes appearing in the later stage of rearrangement. In contrast to this, routes via methylisotwistanes were energetically less favorable compared to those via methylperhydrotriquinacenes. Thus the existence of the latter compounds in the rearrangement product mixture is fully consistent with the theoretical study.

Experimental Section

Isolation of [3.3.3]Propellane (2). A mixture of 60 g (0.4 mol) of *exo-cis*-2,3-tetramethylenenorborane (**1**),[1] 5.4 g (0.04 mol) of anhydrous aluminum chloride, and 400 mL of methylene chloride was heated under reflux for 3 h. The reaction mixture was poured onto 500 mL of ice–water, and the organic layer was separated. The aqueous layer was extracted once with 50 mL of methylene chloride. The combined organic layer and the methylene chloride extract were

washed successively with 2% hydrochloric acid, a saturated sodium bicarbonate solution, and water and dried over anhydrous calcium chloride. Concentration of the solution gave 59 g (98% yield) of the residue which was analyzed on conventional VPC to contain 9.0% of fraction A. This fraction was separated on the preparative VPC: retention time, 7.5 min; column, 3/8 in. $\phi \times 10$ ft, packed with 30% Carbowax 20M on Chromosorb W-AW, at 150 °C; He pressure, 22 lb/in.^{2}; injection port temp, 200 °C; detector temp, 240 °C; 300 μL of the sample being injected every time.

A part (4.5 g, 0.03 mol) of the fraction thus obtained was then heated under reflux with 18.0 g (0.12 mol) of trifluoromethanesulfonic acid in 225 mL of methylene chloride for 16 h. The reaction was quenched by being poured onto 200 mL of ice–water and treated similarly as above to give a dry methylene chloride solution. Concentration of the solution afforded 4.5 g (quantitative yield) of the residue comprising the isomerization products. The residue was fractionated on the preparative VPC, and the first-eluted fraction (fraction A) was recovered to give 0.72 g of crude [3.3.3]propellane (**2**). Purification with slow sublimation in vacuo (~200 mm) yielded 0.58 g (0.97% yield based on **1**) of **2** with 94% purity: mp 116–117 °C; IR (neat) 2920, 2850, 1460, 1440, 1290, 1230, 1200, 1160, 1100, 990, 970, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s). The mass spectrum[1] and the ^{13}C NMR chemical shifts (Table I) were in good agreement with those[3] of an authentic specimen.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.9; H, 12.1.

4-Methylbicyclo[5.2.1]decan-10-one (10). To a solution of 24.0 g (0.21 mol) of 4-methylcyclohexanone (**8**) in 200 mL of a 50:50 v/v mixture of tetrahydrofuran and methanol kept at 2–5 °C was added 2.0 g of anhydrous potassium carbonate and then dropwise with efficient stirring in a period of 7 h a solution of 59.7 g (0.23 mol) of dimethyl *N,N'*-dinitroso-*N,N'*-tetramethylenedicarbamate (**9**) in 1 L of the THF–methanol mixture. The reaction was stirred at the same temperature for an additional 5 h and set aside overnight at ambient temperature. Solid matters were filtered off and the filtrate was concentrated. The residue was extracted with petroleum ether and the solvent was evaporated off. Fractional distillation of the residue gave 7.9 g (21% yield) of a mixture of isomeric 4-methylbicyclo[5.2.1]decan-10-one (**10**), bp 68–70 °C (0.5 mm).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.3; H, 11.0.

The mixture was analyzed on Golay GC–MS to comprise two major constituents (95% of the combined peak areas) in a 58:42 ratio, which were separable also on the preparative VPC. The earlier-eluted, more-abundant component: IR (neat) 2960, 2920, 2860, 1730, 1450, 1370, 1310, 1190, 1140 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ_C 24.20 (t, 2), 28.18 (d, 1), 32.49 (q, 1), 34.44 (t, 2), 35.98 (t, 2), 45.88 (d, 2), 232.04 (s, 0.3); mass spectrum (*m/e*, rel intensity) 166 (43, M$^+$), 151 (32), 112 (53), 110 (32), 109 (33), 97 (37), 96 (37), 95 (43), 84 (34), 83 (33), 82 (32), 81 (50), 68 (32), 67 (43), 55 (100), 54 (32), 41 (55). The later-eluted component: IR (neat) 2960, 2940, 2890, 1740, 1480, 1460, 1440, 1380, 1320, 1140 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ_C 18.03 (q, 1), 24.77 (t, 2), 29.64 (t, 2), 30.62 (d, 1), 31.43 (t, 2), 45.56 (d, 2), 230.09 (s, 0.4); mass spectrum (*m/e*, rel intensity) 166 (44, M$^+$), 123 (38), 112 (60), 110 (38), 109 (38), 96 (40), 95 (47), 84 (37), 83 (40), 82 (38), 81 (62), 68 (37), 67 (50), 55 (100), 54 (34), 41 (61).

4-Methylbicyclo[5.2.1]decan-10-one Tosylhydrazone (11). A solution of 4.3 g (0.026 mol) of the mixture of isomeric 4-methylbicyclo[5.2.1]decan-10-ones prepared above, 5.3 g (0.028 mol) of *p*-toluenesulfonylhydrazine, and 1.0 mL of 35% hydrochloric acid in 200 mL of absolute ethanol was heated under reflux for 3 h, and the reaction was set aside overnight at ambient temperature. Concentration of the solution and recrystallization of the residue from an ethanol–ether (50:50) mixture gave 3.2 g (37% yield) of 4-methylbicyclo[5.2.1]decan-10-one tosylhydrazone (**11**): mp 171–172 °C; IR (Nujol) 3200 (br), 1600, 1170 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}O_2N_2S$: C, 64.65; H, 7.84; N, 8.38; S, 9.57. Found: C, 64.4; H, 7.7; N, 8.6; S, 9.8.

1-Methylperhydrotriquinacene (4). To 66 g of molten acetamide kept at 90–95 °C was added 1.6 g (0.070 mol) of sodium in small portions. After dissolution of the sodium, 5.5 g (0.017 mol) of 4-methylbicyclo[5.2.1]decan-10-one tosylhydrazone (**11**) was added to the solution with efficient stirring, and the reaction temperature was raised to 175 °C in a period of 30 min. The reaction was stirred for 5 min at the same temperature and then cooled down to 90 °C.

To the reaction mixture was added dropwise 55 mL of water, and the resulting mixture was set aside to cool at ambient temperature. The reaction mixture was extracted with three 50-mL portions of *n*-pentane, and the combined pentane extracts were washed with water and dried over anhydrous calcium chloride. Evaporation of the solvent and purification of the residue with the preparative VPC gave 1.7 g (67% yield) of a pure sample of 1-methylperhydrotriquinacene (**4**): mp 33–34 °C; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, $-CH_3$), 0.9–2.2 (complex m); mass spectrum (*m/e*, rel intensity) 150 (22, M$^+$), 135 (15), 107 (30), 95 (15), 94 (100), 81 (44), 80 (21), 79 (22), 67 (14), 41 (14).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.7; H, 12.2.

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Registry No.—**1**, 32789-29-0; **8**, 589-92-4; **9**, 40002-44-6; **10**, *exo*-Me, 23109-52-6; **10**, *endo*-Me, 23109-50-4; **11**, 68796-73-6.

References and Notes

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Photochemical Reaction of Radical ·CMe$_2$X with Toluene[1]

Yoshiro Ogata,* Katsuhiko Takagi, and Eiji Hayashi

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 Japan

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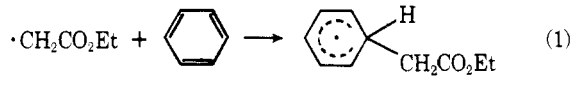
In our previous paper,[2] photodecomposition of ethyl chloroacetate in benzene was found to give a ring substitution product, ethyl phenylacetate, suggesting a radical substitution reaction.



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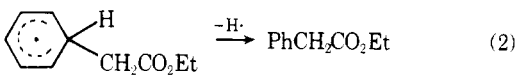

(2)

These types of ring-substituted products were not observed in the thermolysis of azo compounds.[3] To our knowledge, there is only one available report on the photoinduced decomposition of azo compounds in aromatic solvents.[4]

Herein, we report the photodecomposition of AIBN and MAIB in toluene showing a parallelism between the photochemical behavior of MAIB, AIBN, and α-chloroisobutyrate in toluene.

Results and Discussion

Photodecomposition of α,α'-Azobis(isobutyronitrile) (AIBN) in Toluene. Irradiation of 0.10 M AIBN in toluene under N_2 for 4 h gave a mixture (~3%) of α-*p*-tolyliso-

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