$C_{10}H_{19}N_3O_2$: C, 56.31; H, 8.96; N, 19.70. Found: C, 56.43; H, 9.17; N, 19.60.

1-[3-(3-Cyanopentyl)]-2-carbomethoxyhydrazine (6e): needles from cyclohexane, mp 89–91.5 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.05 (t, 6 H), 1.74 (q, 4 H), 3.75 (s, 3 H), 4.02 (s, 1 H), 6.35 (s, 1 H). Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16; N, 22.69. Found: C, 51.98; H, 8.11; N, 22.75.

1-[2-(2-Cyanooctyl)]-2-carbomethoxyhydrazine (6f): leaflets from hexane, mp 45.5–47 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 0.89 (distorted t, 3 H), 1.1–1.9, 1.44 (m, s, total 13 H), 3.76 (s, 3 H), 4.0 (br s, 1 H), 6.4 (s, 1 H). Anal. Calcd for $C_{11}H_{21}N_3O_2$: C, 58.12; H, 9.31; N, 18.49. Found: C, 58.06; H, 9.37; N, 18.61.

1-[2-(4-Methyl-2-cyanopentyl)]-2-carbomethoxyhydrazine (6g): cottonlike crystals from cyclohexane: mp 96–97 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.06 (dd, J = 6.6, 2.9 Hz, 6 H), 1.47 (s, 3 H), 1.66 (dd, J = 8.8, 6.6 Hz, 2 H), 1.9 (m, 1 H), 3.77 (s, 3 H), 4.19 (s, 1 H), 6.48 (s, 1 H). Anal. Calcd for $C_9H_{17}N_3O_2$: C, 54.25; H, 8.60; N, 21.09. Found: C, 54.30; H, 8.68; N, 21.20.

1-(1-Cyanocycloheptyl)-2-carbomethoxyhydrazine (6h): needles from MeOH–H_2O, mp 117–119 °C; IR ν 3410 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.4–2.2 (m, 12 H), 3.7 (s, 4 H), 6.41 (s, 1 H). Anal. Calcd for $C_{10}H_{17}N_3O_2$: C, 56.85; H, 8.11; N, 19.89. Found: C, 56.78; H, 8.11; N, 19.86.

1-(1-Cyano-2-methylcyclohexyl)-2-carbomethoxyhydrazine (6i): rodlike crystals from MeOH–H_2O, mp 139–140 °C (lit.[11b] mp 138 °C); IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.14 (d, J = 5.9 Hz, 3 H), 1.2–1.9 (m complex, 8 H), 2.20 (dd, J = 9.5, 2.9 Hz, 1 H), 3.76 (s, 3 H), 4.0 (br s, 1 H), 6.25 (br s, 1 H). Anal. Calcd for $C_{10}H_{17}N_3O_2$: C, 56.85; H, 8.11; N, 19.89. Found: C, 56.85; H, 8.12; N, 19.73.

1-(1-Cyano-4-*tert*-butylcyclohexyl)-2-carbomethoxyhydrazine (6j): needles from MeOH–H_2O, mp 137–138 °C (lit.[11b] mp 132–133.5 °C); IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 0.88 (s, 9 H), 0.9–1.1 (m, 1 H), 1.42 (m, 4 H), 1.86 (br d, J = 13 Hz, 2 H), 2.16 (br d, J = 13 Hz, 2 H), 3.77 (s, 3 H), 3.8 (br s, 1 H), 6.3 (br s, 1 H). Anal. Calcd for $C_{13}H_{23}N_3O_2$: C, 61.63; H, 9.15; N, 16.59. Found: C, 61.49; H, 9.25; N, 16.57.

1-[2-(2-Cyanonorbornyl)]-2-carbomethoxyhydrazine (6k): cubes from benzene, mp 125–126 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.2–1.7 (m complex, 5 H), 1.84 (d?, J = 11 Hz, 1 H), 1.9–2.2 (m complex, 2 H), 2.36 (br m, 1 H), 2.59 (br m, 1 H), 3.76 (s, 3 H), 4.28 (br s, 1 H), 6.35 (br s, 1 H). Anal. Calcd for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.57; H, 7.25; N, 20.08.

1-(1-Cyanohexyl)-2-phenylhydrazine (8): rhombs from MeOH, mp 101–103 °C; IR ν 3300 (NH), 2220 (CN), 1600 cm^{-1}; ^{1}H NMR δ 1.2–2.2 (m, 10 H), 4.5 (br s, 2 H), 6.8 (m, 3 H), 7.2 (m, 2 H). Anal. Calcd for $C_{13}H_{17}N_3$: C, 72.52; H, 7.96; N, 19.52. Found: C, 72.70; H, 7.92; N, 19.48.

Registry No. **1a**, 24214-79-7; **1b**, 24214-78-6; **1c**, 124243-15-8; **1d**, 124243-16-9; **1e**, 14850-77-2; **1f**, 124243-17-0; **1g**, 124243-18-1; **2a**, 28766-50-9; **2b**, 28766-48-5; **2c**, 124243-19-2; **2d**, 14849-39-9; **3a**, 14702-42-2; **3b**, 14702-41-1; **3c**, 14978-96-2; **3d**, 124243-20-5; **3e**, 68180-96-1; **3f**, 124243-21-6; **3g**, 124243-22-7; **3h**, 88693-07-6; **3i**, 124243-23-8; **3j**, 83859-38-5; **3k**, 124243-24-9; **4a**, 27702-93-8; **4b**, 41857-46-9; **5a**, 27702-91-6; **5b**, 28766-49-6; **6a**, 61827-29-0; **6b**, 124266-40-6; **6c**, 124243-25-0; **6e**, 124243-26-1; **6f**, 124243-27-2; **6g**, 124243-28-3; **6h**, 124243-29-4; **6i**, 61827-30-3; **6j**, 61827-31-4; **6k**, 124243-30-7; **7a**, 766-05-2; **7b**, 4254-02-8; **7c**, 13310-75-3; **7d**, 62391-96-2; **7e**, 617-80-1; **7f**, 2570-96-9; **7g**, 69975-94-6; **7h**, 32730-85-1; *cis*-**7i**, 25144-00-7; *trans*-**7i**, 10479-61-5; *trans*-**7j**, 15619-18-8; *cis*-**7j**, 15619-18-8; *exo*-**7k**, 3211-90-3; *endo*-**7k**, 3211-87-8; **8**, 17643-00-4; **9**, 124243-31-8; **10**, 17643-01-5; **11**, 2094-98-6; **12**, 532-96-7; **13**, 787-84-8; $PhNHNH_2$·HCl, 59-88-1; $PhCONHNH_2$, 613-94-5; $AcNHNH_2$, 1068-57-1; MeO_2CNHNH_2, 6294-89-9; Pr_2CO, 123-19-3; i-Pr_2CO, 565-80-0; Et_2CO, 96-22-0; $MeCO(CH_2)_5CH_3$, 111-13-7; $MeCOCH_2CH(CH_3)CH_3$, 108-10-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; bicyclo[2.2.1]heptan-2-one, 497-38-1.

Novel Reactions of 1-Triptycylcarbinols with Thionyl Chloride–Dimethylformamide

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Reactions of thionyl chloride–dimethylformamide reagent at 58 °C in deuteriochloroform with 1-triptycylcarbinol and ditriptycylcarbinol produced the sulfite ester and the interesting rearranged compound 1-chloro-2-(1-triptycyl)tribenzobicyclo[3.2.2]nonatriene (a triptycyl-substituted homotriptycene), respectively. The mechanistic differences that occur after initial formation of chlorosulfite intermediates are discussed. Molecular mechanics calculations were used to explore the exothermicity of this and related rearrangements.

We wish to report some interesting products from reactions of 1-triptycylcarbinol (**1**) and ditriptycylcarbinol (**2**) with thionyl chloride–dimethylformamide reagent at 58 °C. Ditriptycyl compounds have been studied recently because of interest in "geared" systems,[1] and the rotational barriers for various triptycyl derivatives have been measured and calculated.[2] There have been several attempts to ring expand triptycylmethyl compounds[3] to homotriptycene derivatives. The use of very reactive intermediates in these studies confirmed that bridgehead benzobicyclic carbinyl compounds were very resistant to solvolytic reactions.[4]

Results and Discussion

Our work began with an attempt to prepare ditriptycylmethyl chloride (**3**) from the known[5] **2**. Initial

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(1) Iwamura, H.; Mislow, K. *Acct. Chem. Res.* **1988**, *21*, 175 and references therein.

(2) (a) Imashiro, F.; Terao, T.; Saika, A. *J. Am. Chem. Soc.* **1979**, *101*, 3762. (b) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers, Inc.: Deerfield Beach, FL, 1985; p 269ff.

(3) (a) Cristol, S. J.; Pennelle, D. K. *J. Org. Chem.* **1970**, *35*, 2357. (b) Wilt, J. W.; Malloy, T. P. *J. Org. Chem.* **1972**, *37*, 2781.

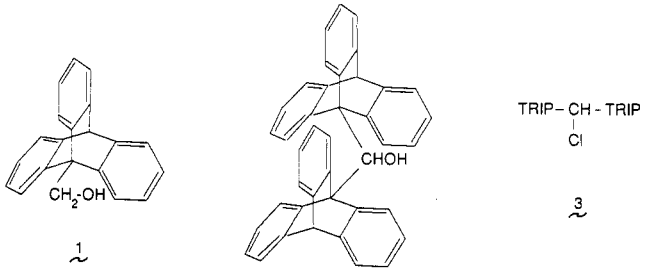
(4) Lancelot, C. L.; Cram. D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 1435 and references therein.

(5) Hounshell, W. D.; Constance D. J.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961.

0022-3263/90/1955-1076$02.50/0

work[6] in an NMR tube indicated no reaction was occurring at 58 °C in deuteriochloroform, but a reaction was observed after some dimethylformamide (DMF) was added to increase reactivity.[7]

Although the white powder isolated in 61% yield after 24 h eluted faster than **2**, had an IR that showed no C–O or OH absorptions, and had a high-resolution mass spectrum with a parent ion for $C_{41}H_{27}Cl$ and loss of chloride as the first decomposition, it was clear from the complicated nature of the aromatic region of the proton NMR spectrum that the expected **3** was not produced. The 300-MHz proton NMR spectrum had a triptycene bridgehead singlet at 5.60 ppm and broadened one-proton singlets at 4.96 and 5.06 ppm, which were shown by a COSY experiment to be coupled to each other. There were some dramatically shielded one-proton aromatic signals that included doublets at 5.30 and 5.75 and triplets at 6.19, 6.46, and 6.68 ppm all with couplings of about 7.6 Hz. These signals appeared to have normal ortho aromatic coupling, and smaller meta couplings of approximately 1.4–1.7 Hz were resolved on most of these signals. Incompletely resolved aromatic multiplets extended from 6.9 to 7.6 ppm and integrated for 19 more protons.

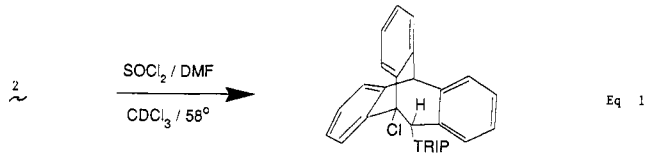


1 2 3

The 75-MHz ^{13}C NMR spectrum revealed three aliphatic methine carbons and two quaternary bridgehead carbon signals. There were 12 quaternary aromatic carbon signals and 23 protonated aromatic carbon signals, one of which was over 50% more intense than the other signals and was thus assigned to two carbons whose signals were coincident. This spectrum clearly does not fit the symmetry of **3** and suggests a remarkably unsymmetrical molecule.

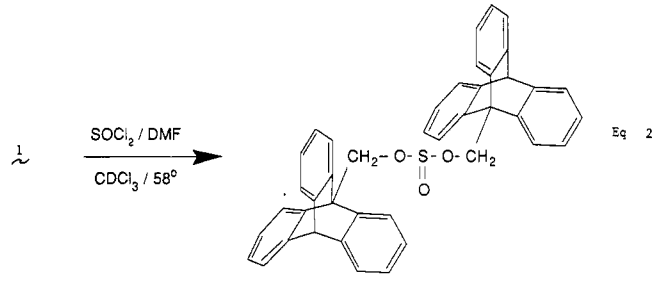
Although the spectroscopic information supports the production of a chloro compound, it is clearly an isomer of the expected **3**. The most probable structure for this new material is the rearranged 1-chloro-2-(1-triptycyl)-tribenzobicyclo[3.2.2]nonatriene (**4**). Inspection of models of **4** showed that two aromatic rings, one from each bicyclic system, are clearly pushed into the adjacent cleft between two aromatic rings on the other bicyclic system. This proximity to the adjacent π systems provides the significant shielding seen in the aromatic region of the proton NMR spectrum. Little transannular π shielding is seen in the normal ditriptycyl methyl derivatives. The interpretation of mutual shielding on two separate rings was reinforced by the COSY results which showed that the aromatic triplet at 6.19 ppm was coupled to the doublet at 5.75 and the triplet at 6.68 and must be due to protons on one aromatic ring. Similarly, the triplet at 6.46 ppm was coupled to the doublet at 5.30 and to a partially resolved triplet at ca. 7.0 and are, therefore, due to protons on a different ring.

The presence of an off-diagonal peak in the COSY between the broadened singlets at 5.11 and 5.02 ppm can be explained by a small homoallylic ^5J coupling[8] across the tribenzobicyclo[3.2.2](homotriptycene) system. Although this coupling is unresolved in a 1D spectrum, it results in broadened signals which are assigned to the bridgehead proton and the proton on the carbon next to the chlorine on the homotriptycene moiety.



4 (61 %)

It was quite surprising to find that this rearrangement occurred so readily in contrast to the much more vigorous conditions used by Cristol[3a] and Wilt[3b] on monotriptycyl methyl systems! In an effort to examine the structural effects on the rearrangement, we decided to react the known[9] 1-triptycylcarbinol (**1**) under the same conditions. The white powder isolated in 75–99% yield after 24 h had a mp >400 °C and eluted on silica more rapidly than **1**. Although the bridgehead proton at 5.40 ppm and the aromatic pattern between 6.9 and 7.4 ppm looked similar to the starting alcohol, the methylene proton signal of this product was a pair of doublets at 5.90 and 5.68 ppm that were deshielded relative to the methylene singlet of starting alcohol **1**. The deshielded pair of doublets suggested a sulfite ester,[10] structure **5**, in which the methylene protons are diastereotopic. This structure was reinforced by the presence of an S–O stretch in the IR spectrum at 1190 cm^{-1}, and the high-resolution mass spectrum which showed a parent ion for $C_{42}H_{30}O_3S$. The carbon spectrum was similar to that of the starting alcohol, but the bridgehead carbons were now better separated. Acidic hydrolysis of **5** affords the starting alcohol **1** in good yield. Neither compound **4** nor **5** has yet produced acceptable crystals for X-ray analysis.



5 (99 %)

Previous mechanistic studies[11–13] have suggested that alcohols react with thionyl chloride to give an intermediate chlorosulfinate which is quickly converted to a sulfite ester by attack of a second alcohol molecule. The chlorosulfinate can be subsequently regenerated in reaction that is catalyzed by chloride ion and is first order[13] in both thionyl chloride and sulfite ester. The production of very different products in our two systems occurs because of different

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(7) Fieser, L. M.; Fieser, M. *Reagents for Organic Synthesis*; J. Wiley: New York, 1967; Vol. 1, p 286 and references therein.
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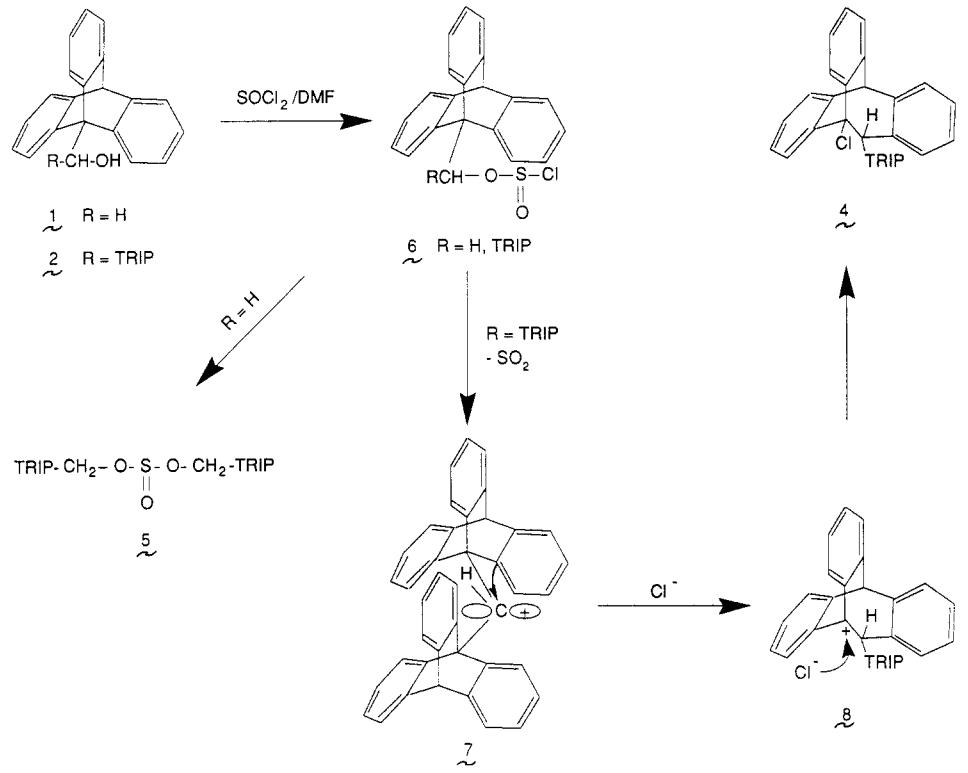
Scheme I



reactions occurring after formation of the chlorosulfinate intermediate.

Thus, we propose that the thionyl chloride–DMF reagent reacts with alcohol **1** to produce a 1-triptycylmethylchlorosulfinate (**6**) (R = H) which is rapidly converted to sulfite ester **5** (see Scheme I). Any subsequent reactions by chloride ion on **5** are inhibited by the bulk of the two large triptycylmethoxy groups. Thus the relatively unreactive **5** is the isolated product. The reaction will proceed without added DMF albeit at a much slower rate. The product yield in this reaction is sensitive to the presence of water, the purity of the thionyl chloride, and the mole ratio of thionyl chloride to starting **1**.

The chlorosulfinate formed from the bulkier ditriptycyl **2** would suffer a different fate because of the greater difficulty of bringing a second mole of **2** close enough to attack the sulfur–chlorine bond of the chlorosulfinate **6** (R = Trip). In the absence of a displacement at carbon or sulfur, thermal cleavage of the chlorosulfinate carbon–oxygen bond would give SO_2, chloride ion, and a poorly solvated and very unstable carbocation **7**. A facile rearrangement could occur very quickly from the tight ion pair. Alternatively, the chloride ion produced in the hydrophobic environment between the triptycenes, would quickly move out to the solvent sheath, returning only after rearrangement. After rearrangement, the less congested and more stable rearranged cation **8** can be trapped by chloride ion to produce the homotriptycene derivative **4** (see Scheme I). Similar ring expansion reactions have been observed for 1-(aminomethyl)triptycene[3a] with nitrosyl chloride or nitrous acid and 1-(aminomethyl)dibenzobicyclo[2.2.2]-octadiene[14] with nitrous acid, but the corresponding alcohol was unreactive with thionyl chloride, HBr, and HBr/$ZnBr_2$.[14]

Overall, the rearrangement is a neophyl rearrangement.[4] The rates for solvolysis of neopentyl and saturated bicyclic bridgehead carbinyl systems have been summarized.[15] Solvolytic rate data on the strained 1-(hydroxymethyl)-benzobicyclo[2.2.1]heptenyl tosylate where π participation is sterically restricted, and a σ-bonded intermediate has been invoked,[4,16] show an inductive retardation of at least 50 for this benzo derivative in comparison to the nonbenzo analogue. The cumulative effect of three β-aryl groups and the lack of solvent assistance on 1-triptycylcarbinyl tosylate made solvolytic rates immeasurably slow even at elevated temperatures.[17] The corresponding triflate is 10^7–10^8 times slower than 1-(hydroxymethyl)bicyclo[2.2.2]octyl tosylate. Wilt found[3b] the 1-triptycylmethyl bromide was quite unreactive, and Cristol reported[3a] the 1-triptycylmethyl chloride unreactive even with silver acetate in acetic acid at 210 °C for 24 h.

Molecular mechanics calculations[18] (Table I) suggest that the energy barrier to the formation of the ditriptycylmethyl carbocation is high. The formation of the high energy chlorosulfinate intermediate circumvents this problem because loss of SO_2 from the high energy **6** (R = Trip) provides a facile pathway to the parent carbocation **7**. Subsequent rearrangement of **7** to the triptycyl–homotriptycyl cation **8** shows a slight increase in strain energy, but the heat of formation for **8** is clearly exothermic, perhaps because the larger ring system allows for better overlap with the two benzo rings.

Calculations for the monotriptycyl system show a similar exothermicity for rearrangment from an intermediate carbocation, but facile attack on the chlorosulfite precursor by a second molecule of alcohol **1** obviates this path. Our

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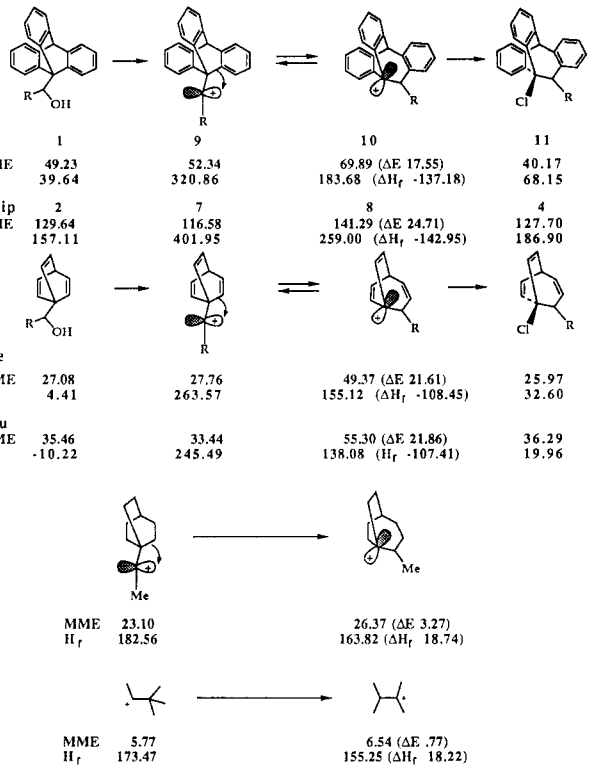
(15) Nordlander, J. E.; Jindal, S. P.; Schleyer, P. v. R.; Fort, R. C.; Harper, J. J.; Nicholas, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 4475 and references cited therein.

(16) Wilt, J. W.; Schneider, C. A.; Berliner, J. P.; Dabek, H. F. *Tetrahedron Lett.* **1966**, 4073 and earlier papers cited therein.

(17) Jarper, J. J.; Imhoff, M.; Schleyer, P. v. R. Reference 4 above, p 1436 and footnote 112.

(18) PCMODEL-2 including π SCF calculations purchased from Serena Software, Box 3076, Bloomington, IN 47402-3076.

Table I. Results from Molecular Mechanics Calculations



calculations on related bicyclo[2.2.2]octatriene systems suggest that the exothermic ring expansion should be general, but the very high activation barrier for ionization prevents a simple solvolytic approach. It is also interesting that the calculated exothermicity for these ring expansions are considerably more negative than those for neopentyl rearrangements, but the neopentyl activation energies are lower. The reactivity of chloride 4 is currently being explored.

Experimental Section[19]

Bis(1-Triptycylmethyl) Sulfite. A 32-μL (0.43-mmol) sample of thionyl chloride was added to 123 mg (0.431 mmol) of 1-triptycylcarbinol in 2 mL of $CDCl_3$ contained in a 5-mm NMR tube. The solution was heated in a 58 °C oil bath for 24 h and then concentrated. The crude product (189.7 mg) was dissolved in benzene and chromatographed on a 15 × 1 cm flash column collecting 20 5-mL fractions of benzene eluent. Fractions 19–20 afforded 4.5 mg of starting carbinol while fractions 1–7 yielded 99 mg (0.16 mmol, 75%) of bis(1-triptycylmethyl) sulfite: mp >400 °C; IR (Nujol) 3070, 1460, 1190 (S-O), 900, 730 cm^{-1}; ^1H NMR (300 MHz) δ 7.5 (6 H, envelope, ArH), 7.38 (6 H, m, ArH), 7.0 (12 H, m, ArH), 5.90 (2 H, d, J = 9.5 Hz), 5.68 (2 H, d, J = 9.5 Hz), 5.40 (2 H, s, bridgehead H); ^{13}C NMR (75 MHz) δ 146.30, 143.63 (Ar quat C's), 125.43, 125.11, 123.67, 121.91 (protonated Ar C's), 60.99 (CH_2O), 54.29 (protonated bridgehead), 52.44 (quat bridgehead); UV 270 (ε = 6560), 278 nm (ε = 7660); mass calcd for $C_{42}H_{30}O_3S$ 614.1916, found 614.1951.

1-Chloro-2-(1-triptycyl)tribenzobicyclo[3.2.2]nonatriene. A 44-μL (0.60-mmol) sample of thionyl chloride and 47 μL (0.61 mmol) of dimethylformamide were added to 81 mg (0.15 mmol) of bis(1-triptycyl)carbinol in 2 mL of $CDCl_3$ contained in a 5-mm NMR tube. After the solution was heated in a 58 °C oil bath for 24 h, it was concentrated. The crude reaction mixture (70.1 mg) was dissolved in benzene and chromatographed on a 15 × 1 cm flash column with collection of 20 5-mL fractions of benzene eluent. Fractions 12–20 afforded 12.0 mg of starting material, while fractions 1–11 afforded 51.2 mg (0.092 mmol, 61%) of the rearranged chloride as a white solid: mp >400 °C; IR (KBr disk) 3060, 2910, 1440, 740, 710, 630, 480 cm^{-1}; ^1H NMR (300 MHz) δ 7.6–6.9 (19 H, m, ArH), 6.68 (1 H, t of d, ArH), 6.46 (1 H, t of d, ArH), 6.19 (1 H, t of d, ArH), 5.75 (d of d, ArH), 5.60 (1 H, s, Trip bridgehead), 5.30 (1 H, d of d, ArH), 5.01 (1 H, s, Homotrip), 4.96 (1 H, s, Homotrip); ^{13}C NMR δ 153.62, 148.68, 147.24, 145.30, 144.54, 144.35, 143.81, 143.44, 141.07, 140.61, 139.00, 136.88 (quat Ar C's), 135.01, 132.95, 127.90, 127.21, 127.03, 126.90 (2 C), 126.82, 126.56, 126.53, 126.40, 125.86, 125.41, 125.33, 125.21, 124.09, 124.04, 123.75, 123.71, 123.51, 123.47, 123.27, 123.22, 121.90 (protonated Ar C's); 63.13, 60.88 (quat aliphatic C's); 56.47, 56.10, 54.03 (protonated bridgehead C's); UV 231 (ε = 3090), 273 (ε = 960), 278 nm (ε = 520, sh); mass calcd for $C_{41}H_{27}Cl$ 554.1800, found 554.1784.

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Registry No. 1, 1469-57-4; 2, 76913-32-1; 4, 124355-00-6; 5, 124355-01-7; 7, 124355-05-1; 8, 124355-08-4; 9, 124355-04-0; 10, 124355-07-3; 11, 24098-04-2; DMF, 68-12-2; $SOCl_2$, 7719-09-7; α-methylbicyclo[2.2.2]octa-2,5,7-triene-1-methanol, 124379-54-0; α-*tert*-butylbicyclo[2.2.2]octa-2,5,7-triene-1-methanol, 124379-55-1; 5-chlorobicyclo[3.2.2]nona-2,6,8-triene, 124355-02-8; 4-*tert*-butyl-5-chlorobicyclo[3.2.2]nona-2,6,8-triene, 124355-03-9; 1-(bicyclo[2.2.2]octa-2,5,7-trien-1-yl)ethylium, 124379-56-2; 4-methyl-1-bicyclo[3.2.2]nona-2,6,8-trienylium, 124355-09-5; 1-(bicyclo-[2.2.2]octa-2,5,7-trien-1-yl)-2,2-dimethylpropylium, 124379-57-3; 4-*tert*-butylbicyclo[3.2.2]nona-2,6,8-trienylium, 124355-10-8; 1-(bicyclo[2.2.2]octan-1-yl)ethylium, 124379-58-4; 2-methylbicyclo[3.2.2]nonan-1-ylium, 124355-06-2; 1,2,2-trimethylpropylium, 20639-76-3; 1,1,2-trimethylpropylium, 17603-18-8.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra of compounds 4 and 5 (12 pages). Ordering information is given on any current masthead page.

(19) All Melting points were taken on a Fisher-Thomas Mel-temp apparatus and are uncorrected. IR spectra were recorded on a Beckman (Acculab 1) spectrometer. Ultraviolet spectra were recorded on a Perkin-Elmer 575 spectrophotometer with ethanol solvent. Proton and carbon NMR spectra were recorded on a Varian VXR-300 in deuteriochloroform and are reported as ppm from tetramethylsilane internal standard. COSY spectra were run using the Varian programs as received and were interpreted from contour plots. All flash columns used silica gel and the procedure of Still et al.[20] Mass spectra were run on a double-focusing MAT 731 spectrometer using electron impact and a direct inlet probe.

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.