and 287. Rate constants for the fast and slow phases of diazepam hydrolysis at 74.5 °C in basic solution are in Table V.

It can be seen that contrary to Han's results, the rate of the first phase was essentially independent of hydroxide concentration, while the second phase was dependent on hydroxide concentration. Reaction in the presence of micelles of CTAB also gave biphasic kinetics, but, in this case, the fast reaction was first order in hydroxide concentration, while the rate of the slow reaction actually decreased slightly as the [OH^-] was increased.

These observations are consistent with a change of mechanism from initial azomethine cleavage in aqueous solution (mechanism **1a** → **3a** → **4a**) to initial amide cleavage in the presence of micelles of CTAB (mechanism **1a** → **2a** → **4a**).

Initial amide cleavage in the presence of micelles of CTAB is indicated by a biphasic reaction in which the rate of the first phase is dependent on [OH^-] (amide cleavage) and the rate of the slower second phase is not increased by increasing [OH^-] (azomethine cleavage in intermediate **2a**).

Initial azomethine cleavage in water is indicated by a biphasic reaction in which the rate of the first phase is essentially independent of [OH^-] (azomethine hydrolysis), while the rate of the slower second phase is dependent on [OH^-] (amide hydrolysis in intermediate **3a**). What remains to be explained is why a reaction involving initial azomethine cleavage at $pH > pK_a$ does not produce monophasic kinetics?

The possibility of recyclization of intermediate **3a** does not necessarily lead to monophasic kinetics if the subsequent breakdown of this intermediate is very slow. We thus achieve a non steady state situation. Intermeidate **3a** accumulates in solution. The first phase is then the establishment of this equilibrium, while the second phase is the slow breakdown of the intermeidate to products.

Since the rate of the second phase of this reaction in water is dependent on the [OH^-], it follows that this is what Han[2] actually observed in his work. The first phase is very fast and could easily have been missed in this original work. If you compare the rate constants obtained by Han at 80 °C in 0.05 M NaOH (4.3×10^{-5} s^{-1}) with our rate constant at 74.5 °C for the second phase of reaction in 0.074 M NaOH (6.8×10^{-5} s^{-1}), this lends support to the above interpretation.

Experimental Section

Materials. Nimetazepam and diazepam were provided by Roche Products Pty. Ltd. *N*-Benzylnitrazepam was available from previous work.[10] Cetyltrimethylammonium bromide (CTAB) (BDH) was purified by the method of Mukerjee and Mysels.[13] Distilled water was further purified by a Millipore system to achieve a resistivity of, at least, 10 MΩ cm^{-1}.

Kinetics. Stock solutions (1×10^{-2} M) of the substrates **1a–d** were prepared in dry dioxane. Stock solutions of NaOH (0.5 M) and CTAB (20 mM) were prepared in purified water. The solutions required for kinetic studies were prepared by mixing appropriate volumes of the stock solutions of NaOH and CTAB and dilution as required. The solutions were placed into cuvettes and allowed 30 min in the constant temperature cell holder of a Varian 634 UV–vis spectrophotometer to reach thermal equilibrium. The temperature within the cuvette was measured with a Jenco thermistor thermometer. Then a sample of the stock solution of the required substrate (12 μL) was added to the cuvette and the contents were mixed thoroughly. The rate of change of absorbance at the desired wavelength was followed by means of a National VP6511A X-T recorder. Repetitive scans of the reaction mixture were obtained with a Hewlett Packard 7041A X–Y recorder.

Reactions were followed to infinity (10 half-lives) where possible or alternatively for very slow reactions or for consecutive reactions an infinity value was calculated by using a computer program designed to give the best straight line fit to data collected over at least 2 half-lives. Good agreement was obtained between rate constants that could be obtained by the two methods. In all cases, the UV–vis spectra of the final products were identical with that of the appropriate substituted 2-aminobenzophenone **4**. Rate constants were all obtained in duplicate and average results are presented in Tables I–V. The reproducibility of the rate constants are all within ±2%.

Acknowledgment. We thank Roche Products (Sydney, Australia) for providing samples of nimetazepam and diazepam.

Registry No. **1a**, 439-14-5; **1c**, 2011-67-8; **1d**, 102725-58-6; **2a**, 102725-59-7; **2c**, 102725-60-0; **2d**, 102725-61-1; **3a**, 36020-94-7; **4a**, 1022-13-5; **4c**, 4958-56-9; **4d**, 37548-92-8; $NH_2CH_2CO_2H$, 56-40-6; cetyltrimethylammonium bromide, 57-09-0.

(13) Mukerjee, P.; Mysels, K. J. *J. Am. Chem. Soc.* **1955**, *77*, 2937.

Synthesis of Tetraisopropylethane and Tetracyclopropylethane and Generation of the Pentacyclopropylethyl Carbocation

Manfred Bruch,[1a,b] Young Moo Jun,[1b] Alan E. Luedtke,[1b] Manfred Schneider,[1a] and Jack W. Timberlake*[1b]

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and FB9 Bergishe Universitat Wuppertal, D-5600 Wuppertal 1, West Germany

Received November 6, 1985

The synthesis of tetracyclopropyl- and tetraisopropylethanes has been achieved through the deazatization of the prerequisite azoalkanes. Variations in reactivity among these azoalkanes support the contention that an isopropyl group is sterically more demanding than a cyclopropyl. The synthesis of pentacyclopropylethane and its conversion to the corresponding carbocation are described.

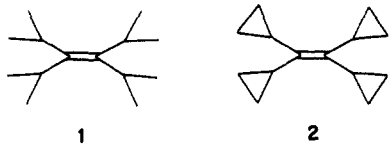
It is clear from comparison of the NMR behavior of tetracyclopropyl- and tetraisopropylethylene that an isopropyl group is considerably more sterically demanding than cyclopropyl. For example, coalescence of the isopropyl groups in **1** occurs at 35 °C[2,3] while no change is noted in **2** at temperatures down to −160 °C.[4] In the synthesis of both tetraisopropyl- and tetracyclopropyl-

(1) (a) Bergishe Universitat Wuppertal. (b) University of New Orleans.

(2) Langler, R. F.; Tidwell, T. T. *Tetrahedron Lett.* **1975**, 777.
(3) Bomse, D. S.; Morton, T. H. *Tetrahedron Lett.* **1978**, 1399.
(4) Nishida, S.; Kataoka, F. *J. Org. Chem.* **1978**, *43*, 1612.

0022-3263/86/1951-2969$01.50/0

ethanes we have encountered precursors that also displayed this steric difference. Furthermore, in the attempted synthesis of tetracyclopropylethane we envisioned intermediates that might readily be converted into the pentacyclopropylethyl carbocation which we wished to study by ^{13}C NMR. A preliminary account of the latter has been reported.[5]



1 2

Results and Discussion

Synthesis of Ethanes. Azoalkanes, through deazatization, are convenient precursors to alkanes.[6] To this end, dicyclopropyl ketazine (**3**)[7] was reduced with lithium aluminum hydride and air oxidized to give a mixture of both cis and trans diazenes **4** (Scheme I). These were identified from both the expected longer λ_{max} for the cis (386 nm vs. 358 nm for trans)[8,9] and the more deshielded methine protons for cis (2.85 vs. 2.05 ppm).[10] The presence of cis was unexpected since normally cis diazenes that have any degree of steric bulk or that can form even moderately stable radicals fragment at relatively low temperatures.[6,9] *cis*-**4** was stable up to 60 °C but decomposed in refluxing heptane to give tetracyclopropylethane. Irradiation at 360 nm in the solid state converted *trans*-**4** to *cis*-**4** and *cis*-**4** to the ethane.

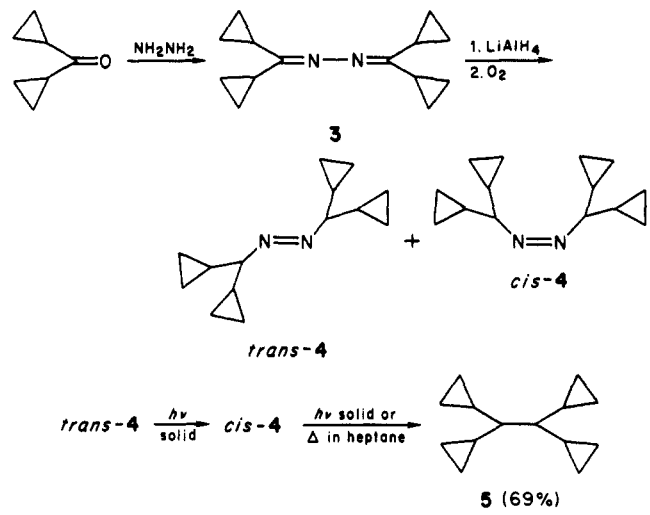
An alternative method of preparation of ethane **5** from tetracyclopropylethylene was also developed. Coupling of dicyclopropyl ketone with a Corey-modified McMurry reagent gives both diol **6** and olefin **2**.[11] The olefin can be converted to epoxide **7** with buffered peracid in moderate yield and the latter proceeds in good yield to ethane **5** with $LiAlH_4/AlCl_3$.[12]

One other obvious route to **5**, the hydrogenation of olefin **2**, led only to ring-opened products even at low pressure (Scheme II).

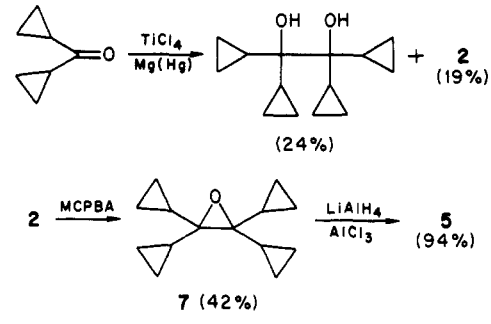
The synthesis of tetraisopropylethane turned out to be considerably more difficult than the cyclopropyl counterpart (Schemes III and IV). Ethylene **1** was prepared with modification of the literature methods.[2,3] However, it proved to be totally inert to high pressure hydrogenation using a variety of catalysts as well as toward diimide (N_2H_2) or BH_3/THF. It could be converted into epoxide **8** but this also proved to be unreactive toward $LiAlH_4/AlCl_3$, either because of the difference in stability of the presumed cationic intermediates (contrast **7**) or because of the greater steric difference between isopropyl and cyclopropyl groups.

Attempts to reduce azine **9** (Scheme IV) and oxidize the hydrazine, following our success with the cyclopropyl analogue **3**, also led to no reaction; this is almost assuredly the result of a steric effect. Addition of chlorine provided the dichloro diazene **10**[13] which was converted in good yield

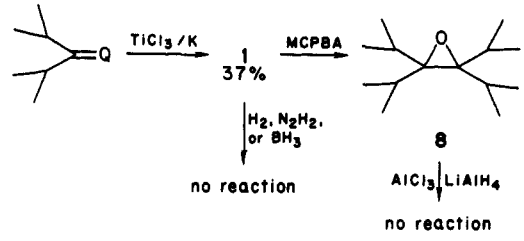
Scheme I



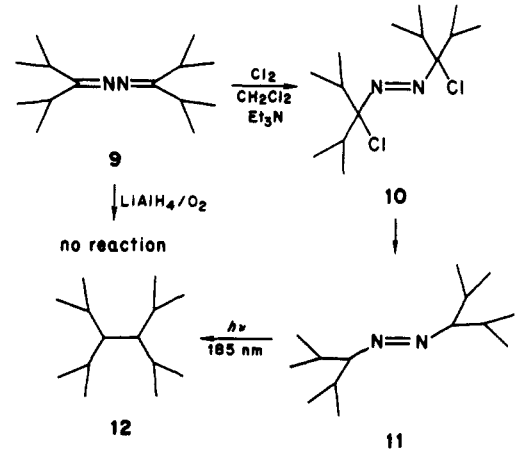
Scheme II



Scheme III



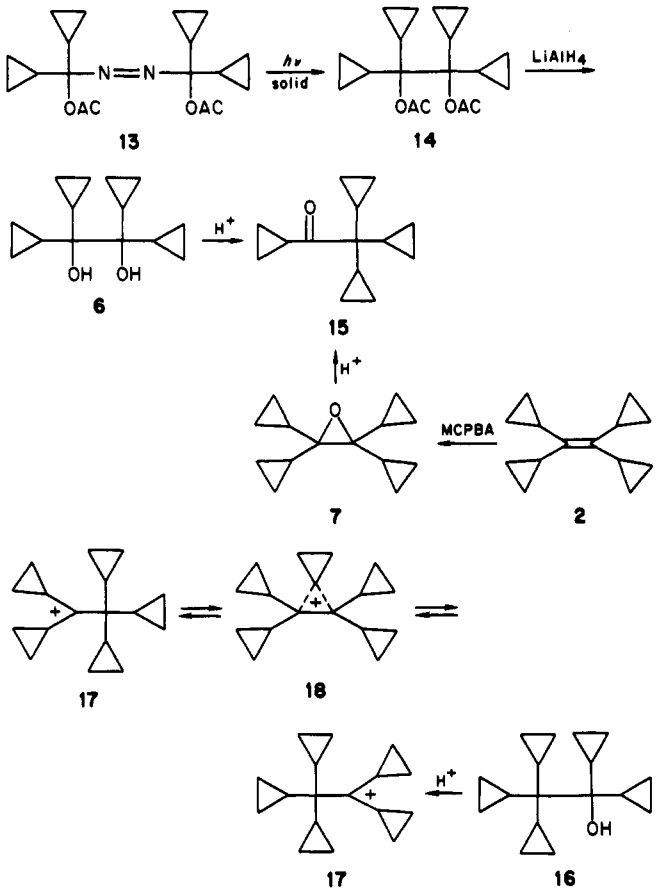
Scheme IV



to the desired azo compound **11**.[14] Here again marked differences were observed between the isopropyl and cyclopropyl derivatives. Compound **11** proved to be a

(5) Jun, Y. M.; Timberlake, J. W. *Tetrahedron Lett.* **1982**, *23*, 1761.
(6) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.
(7) Hart, H.; Curtis, J. E. *J. Am. Chem. Soc.* **1956**, *78*, 112.
(8) Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1976.
(9) Chae, W. K.; Baugham, S. A.; Engel, P. S.; Bruch, M.; Ozmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.
(10) Engel, P. S. *Tetrahedron Lett.* **1974**, 2301; cis and trans azoisopropane methine proton resonate at 3.98 and 3.53 ppm, respectively.
(11) Corey, E. J.; Danheiser, R. L.; Chandrasckaran, S. *J. Org. Chem.* **1976**, *41*, 260.
(12) Timberlake, J. W. *Tetrahedron Lett.* **1970**, 149.
(13) Goldschmidt, S. K.; Acksteiner, B. *Chem. Ber.* **1958**, *91*, 502.
(14) Similar treatment of the dichloro of **3** led to ring-opened products.

Scheme V



"reluctant azo"[6] and did not decompose at 360 nm either in solution or solid state. Fortunately, small quantities sufficient for NMR determination could be prepared by irradiation at 185 nm.

Both ethanes have diastereotopic methyl or methylene carbons as evidenced from their nonequivalency in the ^{13}C NMR, each giving rise to four separate signals. The ^1H NMR (60, 90, and 270 MHz) of tetraisopropylethane also shows the expected separate methyl signals. However, for the tetracyclopropylethane it required high field NMR (400 MHz) to separate the different ring methylene protons and, even here, the two methine protons remain buried under one set of four ring methylene protons. We had hoped that the methine protons might appear upfield of Me_4Si by analogy to tricyclopropylmethane where the methane proton is 30 Hz above Me_4Si.[12] The ring shielding effect in **5** is apparently significantly reduced.

Pentacyclopropylethyl Carbocation. The most logical precursor for the pentacyclopropyl carbocation **17** (Scheme V) appeared to be from pentacyclopropylethanol (**16**). The synthesis of **16** was achieved by addition of cyclopropyllithium to ketone **15**, which was prepared from the pinacol rearrangement of either epoxide **7** or diol **6**. Alternatively, since both diol **6** and olefin **2** (which is the precursor to epoxide **7**) are obtained in low yield from McMurray coupling of dicyclopropyl ketone (Scheme II), we used our previously described method to obtain larger quantities of **6**.[15] This involves the solid state irradiation of azo acetate **13** (Scheme V) to give diacetate **14** (68%) followed by cleavage to give diol **6** (80%), again illustrating the utility of deazatization for coupling reactions.

The pentacyclopropyl carbocation was generated from alcohol **16** at −80 °C in FSO_3H–SbF_5/FSO_2Cl (1:1). The proton-decoupled ^{13}C NMR spectrum shows three signals at δ 125.6, 81.7, and 13.1. Thus all five cyclopropyl rings are magnetically equivalent (down to −100 °C) and display single quaternary, tertiary, and secondary carbon atoms. Similarly the ^1H NMR shows a broad absorption at δ 3.4 for all α-ring protons and another broad absorption for all β-ring protons at 0.3 ppm.

The question as to whether the cation is nonclassical as **18** or whether **18** is a transition state for rapidly equilibrating forms of **17** can be addressed using the Schleyer–Lenoir–Olah[16] technique of comparing the sum of all ^{13}C NMR resonances to that of the corresponding hydrocarbon. This we have done, although comparison to the alcohol **16** rather than hydrocarbon was used in this case since reduction of **16** with $LiAlH_4/AlCl_3$ in an attempt to prepare the hydrocarbon[12] gave ring-opened products. This difference (see Experimental Section) of ~511 ppm falls well within the range of nonclassical ions and on this basis alone **18** is best described as a transition state.

Conclusion

The synthesis of tetracyclopropyl- and tetraisopropylethane has been accomplished by irradiation of the corresponding azo compounds. The different chemical reactivity of several isopropyl and cyclopropyl derivatives helps substantiate the greater steric effect of isopropyl vs. cyclopropyl groups.

Pentacyclopropylethanol has been synthesized and was used to generate the pentacyclopropyl carbocation which shows degenerate cyclopropyl rings in its low temperature ^{13}C and ^1H NMR.

Experimental Section

Dicyclopropyl Ketazine (3). The azine was prepared according to the method of Hart and Curtis.[6]

***cis*- and *trans*-Bis(1,1-dicyclopropylmethyl)diazene (4).** To a suspension of $LiAlH_4$ (8 g, excess) in 150 mL of anhydrous ether was added 9 g (0.04 mol) of dicyclopropyl ketazine (**3**) in 50 mL of ether at −78 °C. The dry ice bath was removed and the reaction mixture was refluxed for 10 h. The excess $LiAlH_4$ was destroyed with 50 mL of ethyl acetate and the mixture was quenched with ice water. Oxygen was bubbled through the solution for 1 h. Extraction with 2 × 250 mL of ether, washing with water, drying ($MgSO_4$), and concentration yielded 4.75 g (52%) of crude product mixture which shows a ratio of cis to trans of 1:4 by ^1H NMR integration at δ 2.85 and 2.02. Separation and purification was accomplished by silica gel chromatography followed by fractional crystallization. *trans*-Bis(1,1-dicyclopropylmethyl)diazene (**4**) was recrystallized from pentane as white needles, 3.75 g (41%): mp 39–40 °C; ^1H NMR (CCl_4) δ 2.02 (t, 2 H), 1.50–0.85 (m, 4 H), 0.52–0.12 (m, 16 H); IR (CCl_4) 3075, 3005, and 2870 cm^{-1}; UV λ_{max} 358 nm (hexane, ε 20.4).

Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.98; H, 10.13; N, 12.68.

The mother liquid was concentrated and the resultant solid was recrystallized from petroleum ether several times, providing 0.8 g (9%) of yellowish white crystals of *cis*-bis(1,1-dicyclopropylmethyl)diazene: mp 116–117 °C; ^1H NMR (CCl_4) δ 2.85 (t, 2 H), 1.57–0.92 (m, 4 H), 0.56–0.12 (m, 16 H); IR (CCl_4) 3075, 3005, and 2870 cm^{-1}; UV (hexane) λ_{max} 386 nm (ε 74.3).

Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.73; H, 10.04; N, 12.59.

Photolysis of *trans*-Bis(1,1-dicyclopropylmethyl)diazene. Cyclopropyldiazene **4** (0.15 g, 0.7 mmol) dissolved in 350 mL of benzene was degassed with nitrogen for 15 min and irradiated with a 200-W Hanovia mercury arc lamp for 5 h. The solvent was removed in vacuo to give a yellow liquid whose NMR spectrum shows ring-opened products: ^1H NMR ($CDCl_3$) δ 1.40–0.85

(15) Timberlake, J. W.; Jun, Y. M. *J. Org. Chem.* **1979**, *44*, 4729.

(16) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(m), 2.60–1.65 (m). (Note, no cyclopropyl ring protons < ~ 0.5 ppm were observed.)

Solid State Photolysis of the Cis Diazene 4. The cis azo **4** (0.50 g, 2.3 mmol) as a finely ground powder was spread on the surface of a glass plate located 5 cm below a 200-W Hanovia lamp. After 2 days of irradiation, the starting material was completely converted to a liquid. Purification on silica gel provided 0.24 g (55%) of 1,1,2,2-tetracyclopropylethane: ^{1}H NMR (CCl_4) δ 1.20–0.70 (m, 4 H), 0.60–0.10 (m, 16 H and 2 H); IR (CCl_4) 3075 (cyclopropyl), 3000, 2860, 1420, and 1455 cm^{-1}; ^{1}H NMR (400 MH_z) δ −0.02 to +0.05 (4 H), 0.07–0.19 (6 H), 0.28–0.37 (4 H), 0.42–0.51 (4 H), 0.89–1.0 (4 H); ^{13}C NMR δ 3.1 (4 C), 4.1 (4 C), 13.8 (4 C), 53.7 (2 C), see Discussion section.

Anal. Calcd for $C_{14}H_{22}$: C, 88.33; H, 11.67. Found: C, 88.03; H, 11.60.

Solid State Photolysis of Trans Azo 4. The procedure followed was the same as for the cis photolysis. Two days of irradiation gave a mixture of cis azo **4** and ethane **5**. However, continuous irradiation of this mixture for two more days converted the *cis*-**4** completely to ethane. From 500 mg of trans azo **4** was obtained 175 mg (40%) of tetracyclopropylethane identical with the sample obtained from above.

Thermal Decomposition of Cis Diazene 4. The cis azo **4** (100 mg, 0.46 mmol) was dissolved in 30 mL of heptane and refluxed for 15 h. Concentration of the solvent and preparatory GC (10% SE-30 on Chromosorb P) yielded 60 mg (69%) of tetracyclopropylethane.

Thermal Decomposition of Trans Diazene 4. The trans azo **4** did not decompose in refluxing toluene and a sample heated in a melting point capillary did not evolve nitrogen until 210 °C. NMR analysis indicated ring-opened products.

Tetracyclopropylethane (5) from Epoxide 7. To a suspension of $LiAlH_4$ (0.79 g, 5 mmol) in 25 mL of ether at 0 °C was added 0.67 g (5 mmol) of $AlCl_3$ in 25 mL of ether. Epoxide **7**, 0.4 g (2.0 mmol), in 25 mL of ether was added and the mixture refluxed for 1 h. The mixture was quenched with water at 0 °C and the organic layer was washed with water, dried, and concentrated to give 0.35 g (94%) of crude product whose spectra were identical with the ethane prepared above.

Procedure for Reductive Ketone Coupling by $TiCl_4$–Mg(Hg). The procedure used was essentially the same as the method of Corey and co-workers,[11] except for some modification in temperature. A suspension of 0.265 g of mercuric chloride in 15 mL of dry THF and 0.80 g of magnesium powder (50 mesh) was stirred for 1 h. The dark gray supernatant was taken off by syringe and an additional 15 mL of THF was added. The suspension was stirred for 1 h at room temperature and cooled to −78 °C followed by addition of 3 g of freshly distilled $TiCl_4$. To the resulting dark suspension was added dicyclopropyl ketone (1 g, 9 mmol) dropwise at 5 °C with stirring for 1 h. The reaction was quenched with 25 mL of 10% NaOH solution and poured onto ice water. Extraction with pentane, washing with water, drying ($MgSO_4$), concentration, and chromatography on silica gel gave 0.48 g (24%) of tetracyclopropylethylene glycol (**6**) and 0.32 g (19%) of tetracyclopropylethylene (**2**).

Tetracyclopropylethylene Oxide (7). To a binary solvent system consisting of 500 mg (23.7 mmol) of tetracyclopropylethylene (**2**) in 20 mL of CH_2Cl_2 and 10 mL of saturated sodium bicarbonate at 0 °C was added 650 mg of *m*-chloroperbenzoic acid in 20 mL of CH_2Cl_2. The reaction was stirred for 12 h. Additional CH_2Cl_2 (50 mL) was added and the organic layer was washed with 10% sodium thiosulfate, saturated sodium bicarbonate, and water. Drying, concentrating, and chromatography on silica gel yielded 230 mg (42%) of a viscous oil identified as epoxide **7**: ^{1}H NMR ($CDCl_3$) δ 1.45–0.80 (m, 4 H), 0.70–0.25 (m, 16 H); IR (CCl_4) 3075 and 3005 cm^{-1}.

Tetraisopropylethylene (1). The olefin was prepared according to the literature in 6% yield: mp 127–128 °C (lit. mp 125–124.5 °C).[2,3] This compound was recovered unchanged from attempted reduction with hydrogen at 2000 psi (Pd/C or Rh/Al), with N_2H_2 or BH_3/THF.[17]

Tetraisopropylethylene Oxide (8). Tetraisopropylethylene (**1**, 1.96 g, 0.01 mol) was dissolved in 100 mL of CH_2Cl_2. To this solution cooled to 0 °C was added 2.30 g of *m*-chloroperbenzoic acid in 50 mL of CH_2Cl_2. The mixture was stirred overnight at room temperature followed by the addition of 300 mL of 10% $Na_2S_2O_3$. Extraction of the organic layer with saturated $NaHCO_3$ (2 × 200 mL) and water followed by drying ($MgSO_4$) and concentration gave a white solid which was recrystallized from pentane to yield 1.75 g (8.25 mmol, 83%) of epoxide: mp 122–123 °C; ^{1}H NMR ($CDCl_3$) δ 0.95 (q, 24 H), 1.95 (m, 4 H); M_r determination 216 (actual 212).

Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.04; H, 13.31.

The epoxide was unreactive toward $LiAlH_4/AlCl_3$ and CH_3MgI but underwent a pinacol rearrangement with H_2SO_4/HOAc to give a product (70%) tentatively identified as 2,5-dimethyl-4,4-diisopropyl-3-hexanone; ^{1}H NMR ($CDCl_3$) δ 0.96–1.12 (m, 24 H), 2.15–2.80 (m, 3 H), 2.85–3.30 (m, 1 H); IR 1700 cm^{-1}.

Diisopropyl Ketazine (9). An autoclave was charged with 4 g (35 mmol) of diisopropyl ketone, 0.56 g (17.4 mmol) of hydrazine, and 50 mL of isopropyl alcohol. It was degassed with nitrogen and heated to 150 °C for 12 h. The solution was poured into 200 mL of water and extracted with pentane, dried, and concentrated to give 3.2 g (80%) of ketazine:[18] ^{1}H NMR ($CDCl_3$) δ 1.04 (d, 12 H), 1.10 (d, 12 H), 2.55 (m, 2 H), 3.17 (m, 2 H); IR (neat) 1625 cm^{-1} (C=N).

The ketazine was unreactive toward $LiAlH_4$ in refluxing ether.

3,3′-Dichloro-2,2′,4,4′-tetramethyl-3,3′-azopentane (10). The chloro azo compound **10** was prepared according to literative methods.[13] From 4.3 g (19 mmol) of diisopropyl ketazine in CH_2Cl_2 at −80 °C was obtained 5.5 g (97%) of **10**: ^{1}H NMR ($CDCl_3$) δ 1.04 (d, 24 H), 2.67 (m, 4 H). This compound was too sensitive to moisture to obtain an analytical analysis and was used directly in the next step.

2,2′,4,4′-Tetramethyl-3,3′-azopentane (11). To a suspension of 1 g (26.3 mmol) of $LiAlH_4$ in 25 mL of THF cooled to 0 °C was added dropwise 1.3 g (4.4 mmol) of chloro azo compound **10** in 15 mL of THF. After refluxing overnight, the solution was quenched with 10 mL of 10% NaOH followed by a addition of 200 mL of water. Extraction with ether, drying ($MgSO_4$), concentration, and column chromatography gave 0.7 g (71%) of 2,2′,4,4′-tetramethyl-3,3′-azopentane (**11**): bp 224–226 °C (from a scaled up run); ^{1}H NMR ($CDCl_3$) δ 0.88 (d, 24 H), 2.14 (m, 4 H), 2.68 (t, 2 H); UV (hexane) λ_{max} 377 nm (ϵ 19).

Anal. Calcd $C_{14}H_{30}N_2$: C, 71.22; H, 14.94; N, 13.84. Found: C, 71.13; H, 14.89; N, 13.72.

Tetraisopropylethane (12). Irradiation of 2,2′,4,4′-tetramethyl-3,3′-azopentane (**11**) at 360 nm (450-W Hanovia) in solution or neat gave no reaction. Irradiation of 147 mg (4.4 mmol) in 25 mL of 2-methylbutane for 3 h at 0 °C at 185 nm and separation by GC resulted in the isolation of 8.5 mg (0.1% yield): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.94 (d of d, 24 H, diastereotopic CH_3 groups coupled to methine J = 7Hz), 1.02 (d of d small impurity), 1.20 (m, 2 H), 1.92 (two nonequivalent pentuplets J = 7 Hz separated by 3.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.8 and 23.5 (diastereotopic CH_3 groups, off resonance two quartets), 27.0 (4 quarternary carbons, off resonance doublet), 49.1 (2 quarternary carbons, off resonance doublet); MS, m/e 198.

1,2,2,2-Tetracyclopropylethanone (15). To 0.4 g (2.0 mmol) of tetracyclopropylethylene oxide (**7**) at 0 °C (no solvent) was added 30 mL of cold formic acid (100%). The reaction was stirred at 0 °C for 8 h, poured onto crushed ice, and extracted with petroleum ether. The extract was washed with 10% $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. Chromatography on silica gel gave 0.25 g (62%) of **15**: ^{1}H NMR ($CDCl_3$) δ 0.20–0.60 (m, 12 H), 0.60–0.75 (m, 3 H), 0.75–0.97 (m, 4 H), 2.22–2.65 (m, 1 H); IR (neat) 3085 and 1695 cm^{-1}. Preparative GC provided a sample with a 5% impurity. The crude product was used in the next step without further analysis.

Under similar conditions tetracyclopropylethylene glycol (0.49 g, 2.2 mmol) gave 0.43 g (95%) of ketone **15**.

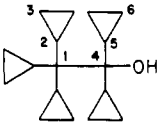
Pentacyclopropylethanol (16). A three-necked, 100-mL flask under argon was charged with 0.5 g (71 mmol) of lithium sand in 20 mL of olefin free hexane. Cyclopropyl bromide (4.0 g, 33 mmol) in 30 mL of hexane was added dropwise and the solution

(17) Rice, J. E.; Okamoto, Y. *J. Org. Chem.* **1982**, *47*, 4189.

(18) Overberger, C. G.; Hale, W. F.; Berenbaum, M. B.; Firestone, A. B. *J. Am. Chem. Soc.* **1954**, *76*, 6185.

was refluxed for 10 h. 1,2,2,2-Tetracyclopylethanone (15, 4.5 g, 22 mmol) in 10 mL of hexane was added dropwise and refluxing was continued overnight. The excess lithium was destroyed with 10 mL of ethanol and the mixture was poured onto ice water. Extraction with ether, washing with water, drying ($MgSO_4$), and concentration resulted in a viscous oil which solidified upon distillation: bp 136–141 °C (1 mm); recrystallization from pentane gave 1.55 g (28%) of tetracyclopropylethanol: mp 33–34 °C; ^1H NMR ($CDCl_3$) δ 0.12–0.69 (m, 20 H), 0.71–0.98 (m, 3 H), 1.21–1.53 (m, 2 H), 1.89 (s, 1 H), NMR data is incorrectly reported in ref 5; ^{13}C NMR ($CDCl_3$) 0.0 (C-3), 1.5 (C-6), 10.5 (C-2), 15.0 (C-5), 43.0 (C-1), 77.1 (C-4); IR (CCl_4) 3590, 3475, 3075, and 2860 cm^{-1}.

Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.76; H, 10.65.



Pentacyclopropylethyl Carbocation (17). To a mixture of $HFSO_3$–SbF_5 (Aldrich) and FSO_2Cl (1:1 v/v) at −80 °C in a glovebag under nitrogen was added dropwise 150 mg of alcohol 16 in 0.5 mL of FSO_2Cl from a precooled pipet. The mixture was transferred to a 5-mm precooled NMR tube which was sealed and transferred to a 10-mm NMR tube containing 3 mL of acetone-d_6 for the lock signal: ^1H NMR (super acid) δ 0.3 (m, 20 H), 3.4 (bs, 5 H); ^{13}C NMR (super acid) δ 13.1 (2° C), 81.7 (3°), 125.6 (4°).

The calculation to determine nonclassical or classical nature was determined according to the Schleyer–Lenoir–Olah method.[16] $\Delta\Sigma\delta_{C^+,\delta CH}(ppm) = \Sigma\delta_{C^+}(ppm) - \Sigma\delta_{CH}(ppm) = 125.6 \times 2) + (81.3 \times 5) + (13.1 \times 10) - [(10.5 \times 3) + 43.0 + 77.1 + (15.0 \times 2) + (1.5 \times 4) + (40$, average correction for alcohol to hydrocarbon[19])]. For nonclassical ions the values are reported to be 270–325 ppm,[16] well below the value of 511 ppm calculated here.

Acknowledgment. M.S. and J.W.T. thank the North Atlantic Treaty Organization (NATO) for a collaborative Research Grant. We also acknowledge the assistance of Dr. Cecil Charles in obtaining the 400-MHz NMR septrum.

Registry No. 1, 7090-88-2; 2, 23534-93-2; 3, 15813-18-0; *cis*-4, 100515-65-9; *trans*-4, 100515-66-0; 5, 102652-65-3; 6, 37614-40-7; 7, 82701-08-4; 8, 4468-67-1; 9, 15813-19-1; 10, 52406-51-6; 11, 102652-66-4; 12, 102652-67-5; 15, 82701-09-5; 16, 82701-10-8; 17, 82701-11-9; dicyclopropyl ketone, 1121-37-5; 2,5-dimethyl-4,4-diisopropyl-3-hexanone, 54580-25-5; diisopropyl ketone, 565-80-0; cyclopropyl bromide, 4333-56-6.

(19) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

Photochemical Transformations. 43. Ionic and Di-π-methane Photochemistry of Some Benzylic Derivatives of Benzobicyclo[3.2.1]octadienes[1]

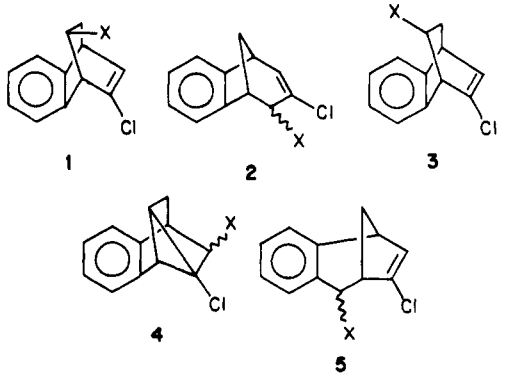
Stanley J. Cristol* and Wayne A. Dickenson

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Received October 17, 1985

exo- and *endo*-7-chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-2-ols (5-OH) give stereospecific di-π-methane rearrangements to *exo*- and *endo*-7-chloro-3,4-benzotricyclo[4.1.1.$0^{5,7}$]oct-3-en-2-ols (6-OH and 7-OH), respectively, under direct and triplet-senstized irradiations. *exo*-4,6-Dichloro-2,3-benzobicyclo[3.2.1]octa-2,6-diene (*exo*-5-Cl) gives an analogous di-π-methane rearrangement to 6-Cl under triplet-sensitized conditions. In addition, under both direct and sensitized irradiation, it gives ionic (solvolysis and epimerization) products. These include, in aqueous acetonitrile (direct), *endo*-5-Cl, *exo*-5-OH, and *exo*-5-$NHCOCH_3$, in aqueous acetonitrile (sensitized with benzophenone or acetone), *exo*-5-OH and *exo*-5-$NHCOCH_3$, and in aqueous acetone, *exo*-5-OH. The sensitized irradiations also lead to the homoallyl-to-cyclopropylcarbinyl rearrangement product, *exo*-6,7-dichloro-3,4-benzotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (*anti*-4-Cl).

Some years ago,[2] members of our research group began a study of the ground-state and excited-state interactions of the chlorobenzobicyclo[2.2.2]octadienyl and -[3.2.1]octadienyl systems and the chlorobenzotricyclo[3.2.1.$0^{2,7}$]-octene system. It was shown that ground-state reactions interconverted 1 and 2 species by anti (antarafacial) migrations. Similarly, species 3–5 were interconverted by ground-state reactions. No mixing of systems occurred. It was also shown that photolyses of 2-Cl and 2-OMs epimers in acetic acid or in acetonitrile–water led to 2-solvolysis products, to epimerization, and to rearrangement to 1-Cl (or 1-OMs) species. Irradiation of *anti*-4-Cl and *anti*-4-OMs led to 5 solvolysis products and 5 isomers,[3] while the *syn*-4 epimers were inert. Irradiation of 1-Cl also led[4] to 5 (syn migration) as principal products, although



about 30% of the anti migration products 2 were also produced. The syn [2.2.2] epimer 3 was photoinert.

While the direct irradiation of 2-OMs epimers led to "ionic" photochemistry (solvolysis and Wagner–Meerwein

(1) Paper 42. Cristol, S. J.; Braun, D.; Schloemer, G. C.; Vanden Plas, B. *Can. J. Chem.*, in press.

(2) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707.

(3) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.

(4) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218.

0022-3263/86/1951-2973$01.50/0