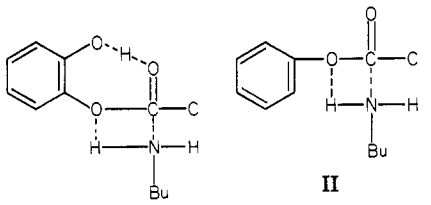
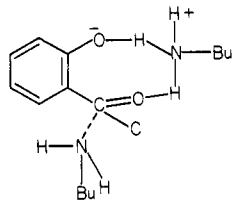


I

II



III

was dried over sodium and distilled. Catechol monoacetate was made by the method of Hansen.[5] Hydroquinone monoacetate was made by treating a basic solution of hydroquinone with acetic anhydride[6] and recrystallization from Skellysolve B. Other chemicals were made and/or purified by standard procedures.

Methods. The experimental procedures previously described[1] were used here. The hydrogen-bonding studies were made with a Perkin-Elmer 521 infrared spectrophotometer.

Third-order rate constants were calculated from the equation

$$k_3t = \frac{1}{(b-a)}\left[\frac{x}{a(a-x)} + \frac{2.303}{(b-a)}\log\frac{b(a-x)}{a(b-x)}\right]$$

which was erroneously printed in ref 1.

Acknowledgment. We express our appreciation to the East Tennessee State University Research Development Committee for partial support of this paper.

Registry No. Catechol monoacetate, 2848-25-1; methyl *o*-hydroxyphenylacetate, 22446-37-3; methyl *p*-hydroxyphenylacetate, 14199-15-6; *n*-butylamine, 109-73-9.

(5) Hansen, B. *Acta Chem. Scand.* **1963**, *17*, 1375.
(6) Chattaway, F. D. *J. Chem. Soc.* **1931**, 2495.

Tetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecane (2,9-Ethanonoradamantane) and 12-Oxapentacyclo[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]dodecane Systems

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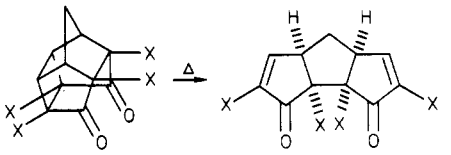
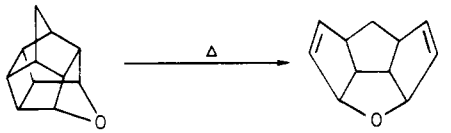
Received December 28, 1982

Recently, we reported an efficient and versatile synthetic approach to all-*cis* triquinane bis enones of type **2** and oxatetraquinane of type **4** via the thermal [2 + 2] cycloreversion of pentacyclic undecanedione **1** and the hexacyclic caged ether **3**, respectively.[1] Herein, we describe facile transskeletal cyclization reactions of **2** and **4**, which paves the way for gainful entry into the interesting polycyclic system **5** and **6** mentioned in the title.[2-4] The

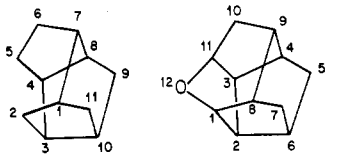


1a, X = H
b, X = Cl

2a, X = H
b, X = Cl



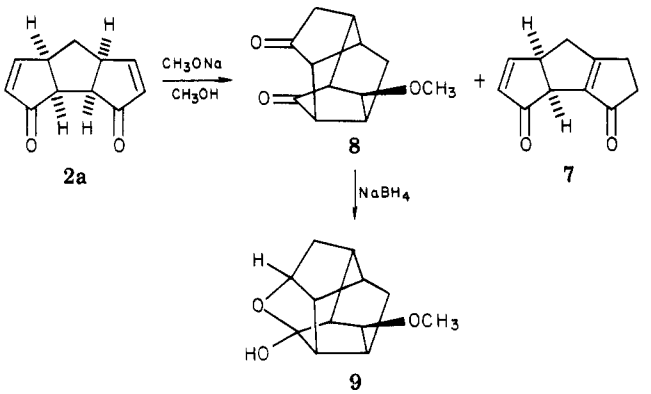
3 **4**



5 **6**

structural similaries between **5** and **6** is quite apparent, and the latter is derived simply through the insertion of an oxygen bridge between the two spatially proximate carbon atoms C_2 and C_5 of **5**. There is considerable interest in these and related ring systems, and they are in fact scarcely accessible.[2-4]

Exposure of **2a** to excess sodium methoxide in methanol furnished a 4:3 mixture of two crystalline products. The minor product was readily recognized as the isomerized bis enone **7** with relocated double bond.[1b] The major



2a **8** **7**

9

product, mp 148-149 °C, was analyzed for $C_{12}H_{14}O_3$ and indicated incorporation of methanol into the product. Its ^{1}H NMR spectrum (δ 3.29, 3 H, s) confirmed this surmise and showed the absence of any olefinic proton resonances. The only other clearly discernible resonance in the ^{1}H NMR spectrum was the presence of a singlet at δ 3.52 due to the proton attached to the carbon bearing the methoxy group. This was corroborated by the ^{13}C NMR spectrum, which exhibited resonances at δ 83. (d) due to the methoxy-bearing carbon and at δ 55.5 (q) due to the methoxy carbon. The absence of any olefinic carbon resonances established the tetracyclic nature of the product. The IR spectrum (1750 cm^{-1}, br) and ^{13}C NMR resonances at δ 214.5 (s) and 211.4 (s) showed the remaining two oxygen

(1) (a) Mehta, G.; Reddy, A. V.; Srikrishna, A. *Tetrahedron Lett.* **1979**, 4863. (b) Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543.

(2) Only one preparatively useful, multistep approach to the tetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecane (2,9-ethanonoradamantane) system has been reported in literature from *exo*-2-noradamantanol.[3] The pentacyclic ether **6** to our knowledge remains unknown. However, synthesis of several oxadiamantanes related to **6** have been reported recently.[4]

(3) Godleski, S. A.; Schleyer, P. v. R.; Osawa, E.; Inamoto, Y.; Fujikura, Y. *J. Org. Chem.* **1976**, *41*, 2596.

(4) Ammann, W.; Jaggi, F.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 2019. Doecke, C. W.; Garratt, P. J. *Tetrahedron Lett.* **1981**, *22*, 1051.

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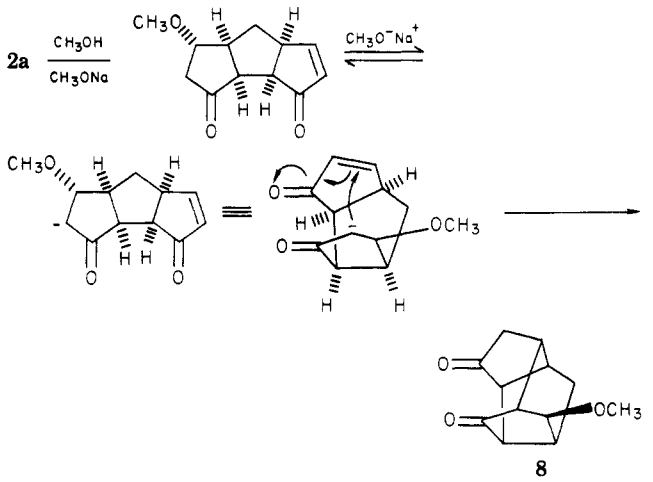
Scheme I

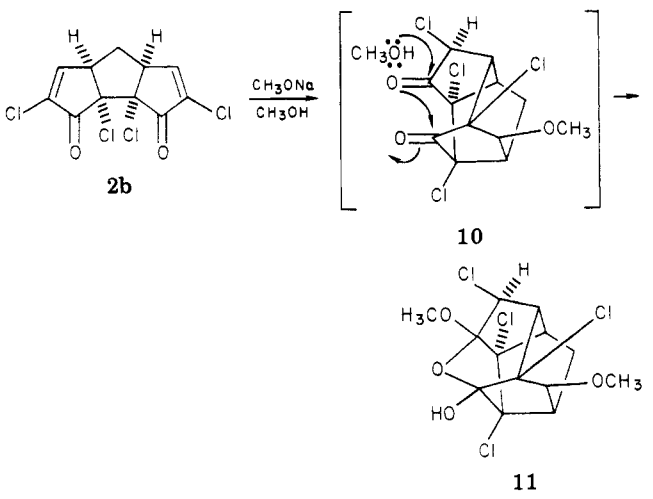


8

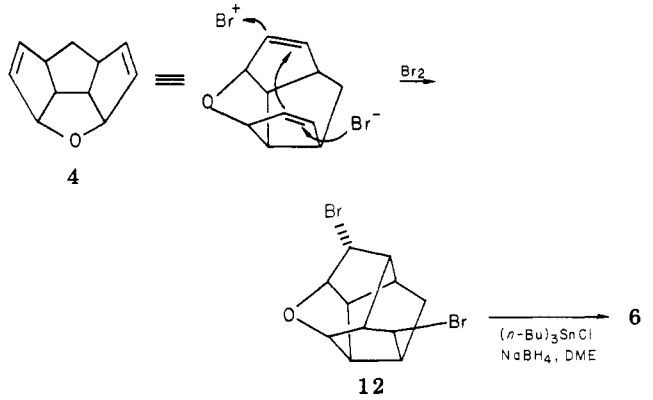
atoms in the molecule to be present as part of the cyclopentanone substructure. All the foregoing spectral data in conjunction with mechanistic considerations indicated the tetracyclic structure **8** as the major product. Firm support for formulation **8**, which also revealed the proximity of the two carbonyl groups, was forthcoming from the controlled $NaBH_4$ reduction to furnish hemiacetal **9**, mp 54–55 °C, in quantitative yield. A plausible mechanism involving sequential inter- and intramolecular Michael additions is depicted in Scheme I. The stereochemistry of the methoxy group in **8** follows from the preferred addition of methanol to folded **2a** from the convex face.

The tandem Michael additions (Scheme I) to bis enone **2a** seems to be a general reaction of this type of all cis, bis enones. For example, tetrachloro bis enone **2b** on treatment with methanolic sodium methoxide yielded a single crystalline compound, mp 207 °C, in 65% yield. The elemental analysis of $C_{13}H_{14}Cl_4O_4$ indicated the addition of two molecules of methanol. The IR spectrum was devoid of any carbonyl absorption but had a broad discrete hydroxyl absorption at 3390 cm^{-1}. The addition of two molecules of methanol was firmly established by the ^1H NMR spectrum (3 H singlets at δ 3.63 and 0.55), which also exhibited a singlet at δ 5.06 (1 H, exchangeable with D_2O), a doublet at δ 4.09 (1 H), and a singlet at δ 3.25 (1 H). The three resonances were readily assigned to the proton at the hydroxyl, the proton attached to the carbon-bearing chlorine, and the proton attached to the carbon bearing the methoxyl group, respectively. The ^{13}C NMR spectrum confirmed the presence of all three functionalities and in addition showed quaternary carbon singlets at δ 109.6 and 105.2 characteristic of hydroxy ether (-OC(OH)<) and methoxy ether (-OC(OCH_3)<) functionalities.[5] These spectral features, and the fact that two molecules of methanol have been added, led to the structural formulation **11**. It would seem that the initially formed product **10** of inter- and intramolecular Michael addition of methanol to **2b** further adds methanol transannularly to the proximate carbonyl groups to furnish **11**.[6] The stereochemistry at C_{10} (-CHCl) of **11** follows from the preferred protonation from the exo face.

While entry to the 12-oxapentacyclo-[6.4.0.$0^{2,6}$.$0^{3,11}$.$0^{4,9}$]dodecane system of **6** could be realized through transannular addition to the proximate carbonyl groups (e.g., formation of **9** and **11**), a more direct entry



to this ring system and the parent compound **6** itself was achieved from the oxatetraquinane **4**. Addition of 1 mol



of bromine to **4** led to a dibromo compound, $C_{11}H_{12}OBr_2$, mp 54–55 °C, as the only isolable product of the reaction. The structure **12** for this product, derived through transskeletal cyclization, followed from its ^1H and ^{13}C NMR (11 lines indicating absence of symmetry as well as unsaturation) data summarized in the Experimental Section. Reductive dehalogenation of **12** with tri-*n*-butyltin hydride, generated in situ,[7] furnished the highly volatile, waxy, pentacyclic ether **6**, mp 198–199 °C. The ^{13}C NMR spectrum of **6** had resonances at δ 86.5 (d), 79.8 (d), 55.1 (d), 51.8 (d), 49.6 (d), 41.27 (t), 41.07 (2c, td), 39.6 (d), 37.3 (t), and 35.5 (d) and was in complete agreement with its formulation.

Experimental Section

All melting points were recorded on a Buchi SMP-20 apparatus and are uncorrected. Boiling points refer to bath temperatures. IR, ^1H NMR (100 MHz), ^1H NMR (270 MHz), and ^{13}C NMR (25.0 MHz) spectra were recorded on a Perkin-Elmer 297 spectrophotometer, a Jeol MH-100 spectrometer, a Brucker 270-MHz spectrometer, and a Jeol FX-100 spectrometer, respectively. ^1H and ^{13}C NMR chemical shifts are given in the δ scale with Me_4Si as internal standard. In the ^{13}C NMR spectra, off-resonance multiplicities, when recorded, are given in parentheses. The standard abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Elemental analyses were carried out on a Hewlett-Packard 185-B CHN analyzer. High-resolution mass measurements were carried out on a AEI MS-5076 mass spectrometer. Analytical thin-layer chromatographies (TLC) were performed on (10 × 5 cm) glass plates coated (250 μm) with Acme's silica gel G (containing 13% calcium sulfate as binder). Visualization of the spots was achieved by exposure

(5) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

(6) We cannot fully rule out the structure for **11** with the positions of hydroxyl and methoxyl groups interchanged on the basis of spectral data.

(7) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* 1982, *104*, 774.

to iodine vapor. Acme's silica gel G (100–200 mesh) was used in the column chromatography. Petroleum ether refers to fraction between 60 and 80 °C. All solvent extracts were washed with brine, dried over Na_2SO_4, and dried on a Buchi-El rotary evaporator under reduced pressure.

Reaction of Tricyclo[6.3.0.0^{2,6}]undeca-4,9-diene-3,11-dione (2a) with Sodium Methoxide. To an ice-cold, magnetically stirred solution of bis enone **2a** (175 mg, 1 mmol) in 5 mL of absolute methanol was added sodium methoxide (200 mg, 3.6 mmol) in small portions over a period of 5 min. The cooling bath was removed and the reaction mixture was stirred at room temperature for 10 min. Most of the methanol was removed under reduced pressure, and the reaction mixture was diluted with water (15 mL). Acidification with dilute HCl, extraction with dichloromethane (15 mL × 3), and usual workup furnished 170 mg of crude material. This material was charged on a silica gel (10 g) column and chromatographed. Careful elution with 20% ethyl accetate–benzene furnished 65 mg (40%) of 11-methoxytetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecane-2,5-dione (**8**), which was crystallized from dichloromethane–petroleum ether: mp 148–149 °C; IR (KBr) 1745 cm^{-1} (carbonyl); ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.52 (1 H, s, *H*COCH$_3$), 3.29 (3 H, s, OCH$_3$), 2.84 (3 H,br s, bridgehead CH), 2.65 (3 H, br, s, bridgehead CH), 2.3 (2 H, m, CH$_2$C(O)-), 1.9–2.2 (2 H, m, CH$_2$); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 214.5 (s) and 211.4 (s) (>C=O), 83.1 (d, *C*HOCH$_3$), 64.6 (d), 57.7 (d), 55.5 (q, OCH$_3$), 51.7 (d), 47.3 (d), 45.6 (t, *C*H$_2$C(O)-), 41.0 (d), 39.6 (d), 36.1 (t). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.95; H, 6.74.

Further elution of the column with 40% ethyl acetate–benzene furnished 35 mg of the unreacted starting material. Final elution of the column with ethyl acetate furnished 42 mg (30%) of tricyclo[6.3.0.0^{2,6}]undeca -1(8), 4-diene-3,11-dione (**7**), which was identified by comparison (TLC, GLC, and IR) with an authentic sample.[1b]

Reaction of 11-Methoxytetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecane-2,5-dione (8) with Sodium Borohydride. To an ice-cold, magnetically stirred solution of dione **8** (50 mg, 0.24 mmol) in 5 mL of methanol was added sodium borohydride (15 mg, 0.4 mmol). The cold bath was removed, and the reaction was stirred at room temperature for 15 min and quenched with 2 drops of acetone. The solvent was removed under reduced pressure, and the contents of the flask were diluted with water and extracted with dichloromethane (10 mL × 2). The organic extract was washed and dried and the solvent removed to furnish 50 mg (100%) of 7-methoxy-12-oxapentacyclo[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]dodecan-1-ol (**9**). Bulb-to-bulb distillation (130 °C (0.6 mm)) followed by crystallization from petroleum ether furnished the crystalline compound: mp 54–55 °C; IR (KBr) 3270 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 4.96 (1 H, s, exchangeable with D_2O), 4.56 (1 H, br s), 3.37 (4 H, s), 2.95 (1 H, m), 2.4–2.7 (2 H, m), 1.2–2.3 (7 H, en); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 113.4 (s), 91.2 (d), 77.1 (d), 56.0 (q), 55.4 (d), 54.2 (d), 48.6 (d), 47.6 (d), 40.7 (d), 40.4 (t), 40.2 (d), 38.6 (t); high-resolution mass spectrum *m/e* M$^+$ calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1098.

2,3,8,10-Tetrachloro-1(or 11),7-dimethoxy-12-oxapentacyclo[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]dodecan-11(or 1)-ol (11). To an ice-cold, magnetically stirred solution of tetrachloro bis enone **2b** (500 mg, 1.6 mmol) in 15 mL of absolute methanol was added sodium methoxide (200 mg, 3.6 mmol) in small portions over a period of 5 min. Most of the methanol was removed under reduced pressure, and the reaction mixture was diluted with water, acidified with dilute HCl, and extracted with dichloromethane (30 mL × 2). The organic extract was washed and dried. Evaporation of the solvent and filtration through a small silica gel (10 g) column using 5% ethyl acetate–benzene furnished 400 mg (65%) of **11**, which was crystallized from dichloromethane–petroleum ether; mp 207 °C; IR (KBr) 3390 cm^{-1} (hydroxyl); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.06 (1 H, s, exchanged with D_2O, OH), 4.0 (1 H, d, *J* = 3.3 Hz, *H*CCl), 3.63 (3 H, s, OCH$_3$), 3.55 (3 H, s, OCH$_3$), 3.25 (1 H, s, *H*COCH$_3$), 2.82 (1 H, t, *J* = 3.3 Hz), 2.75 (1 H, dd, J_1 = 7 Hz, J_2 = 2.5 Hz), 2.5–2.7 (1 H, m), 2.54 (1 H, m), 1.89 (1 H, dd, J_1 = 12.5 Hz, J_2 = 1.1 Hz); ^{13}C NMr (25.0 MHz, acetone-d_6) δ 109.6 (s, >C(OCH$_3$)o-), 105.2 (s, >C(OH)O-), 91.2 (d, *C*HOCH$_3$), 86.9 (s), 83.8 (s), and 69.9 (s) (CCl), 59.9 (d), 59.1 (d), 55.1 (q?), 52.8 (q, OCH$_3$), 51.1 (d), 50.4 (d), 35.5 (t, CH$_2$). Anal. Calcd for $C_{13}H_{14}Cl_4O_4$: C, 41.49; H, 3.72. Found: C, 41.46; H, 3.69.

7,10-Dibromo-12-oxapentacyclo[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]dodecane (12). To an ice-cold, magnetically stirred solution of **4** (300 mg, 1.87 mmol) in CCl_4 (10 mL) was added bromine (300 mg, 1.87 mmol) in 3 mL of CCl_4, drop by drop, over a period of 20 min. The reaction mixture was allowed to warm up and stirred at room temperature for another 10 min. Carbon tetrachloride was removed under reduced pressure, and the crude residue (400 mg) was purified by a quick filtration through a silica gel (10 g) column and crystallized from petroleum ether on long standing at 0 °C to furnish the dibromo compound **12** (330 mg, 54%): mp 54–55 °C; IR (KBr) 1210, 1080, 840, 730 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.18 (1 H, br s, HCO-), 4.68 (1 H, d, HCO-), 4.36 (1 H, s, HCBr), 4.06 (1 H, s, HCBr), 3.2–2.76 (4 H, br m), 2.56–2.32 (2 H, br s), 2.2–2.04 (2 H, br m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 85.6 (d), 85.5 (d), 59.1 (d), 58.8 (d), 53.7 (d), 50.9 (d), 50.2 (d), 47.4 (d), 45.8 (d), 41.2 (t); high-resolution mass spectrum, *m/e* M$^+$ calcd for $C_{11}H_{12}OBr_2$ 317.9256, no M$^+$ detected, 239.0065 (m − Br)$^+$.

12-Oxapentacyclo[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]dodecane (6). The dibromo compound **12** (200 mg, 0.62 mmol) in 10 mL of dry DME was placed in a three-necked, round-bottomed flask flushed with dry nitrogen. To the stirred solution was added tri-*n*-butytin chloride (135 mg, 0.41 mmol) followed by sodium borohydride (200 mg, 5.2 mmol). The reaction mixture was refluxed for 24 h, cooled to room temperature, and diluted with ether (25 mL). The ethereal layer was washed with brine and dried. Evaporation of the solvent gave 200 mg of crude product, which was directly sublimed (70 °C (≃30 mm)) to furnish 12-oxapentacyclo-[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]dodecane (**6**, 50 mg, 50%): mp 198–199 °C; IR (KBr) 2950, 1080 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 4.59 (1 H, unresolved triplet, *J* = 5 Hz), 4.24–4.14 (1 H, br m), 3.0–2.52 2.52 (2 H, br m), 2.52–2.28 (1 H, m), 2.28–1.2 (9 H, m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 86.5 (d), 79.8 (d), 55.1 (d), 51.8 (d), 49.6 (d), 41.27 (t), 40.07 (2c), 39.6 (d), 37.3 (t), 35.5 (d); high-resolution mass spectrum, *m/e* M$^+$ calcd for $C_{11}H_{14}O$ 162.1045, found 162.1038.

Registry No. 2a, 82217-29-6; **2b**, 73843-53-5; **4**, 82253-76-7; **6**, 87453-44-9; **7**, 82253-89-2; **8**, 87453-45-0; **9**, 87453-46-1; **11**, 87453-47-2; **12**, 87453-48-3.

Bromine-Initiated Rearrangement of 4-Homoadamantanone Ethylene Dithioketal

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Received May 24, 1983

In the course of our studies in homoadamantane chemistry[1] we investigated bromination of 4-homoadamantanone ethylene dithioketal (**1**). The product was an olefin, 4,5-[(thioethano)thio]-4-homoadamantene (**2**)! According to our knowledge such a reaction of an ethylene dithioketal with bromine is unprecedented.

Dithioketal **1** was prepared in 79% yield from 4-homoadamantanone[2] by the usual procedure.[3] Treatment of

(1) (a) Majerski, Z.; Hameršak, Z. *Tetrahedron Lett.* **1978**, 3291. (b) Majerski, Z.; Hameršak, Z.; Škare, D. *Ibid.* **1977**, 3943. (c) Mlinarič-Majerski, K.; Majerski, Z.; Pretsch, E. *J. Org. Chem.* **1976**, *41*, 686. (d) *Ibid.* **1975**, *40*, 3772. (e) Hameršak, Z.; Škare, D.; Majerski, Z. *J. Chem. Soc., Chem. Commun.* **1977**, 478. (f) Osawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361. (g) Janjatovič, J.; Škare, D.; Majerski, Z. *J. Org. Chem.* **1974**, *39*, 651.

(2) Schleyer, P. v. R.; Funke, E.; Liggero, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 3965.

(3) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 356.

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