temperature and vented. The reaction mixture was transferred to a 25-ml flask and the liquid portion transferred on a high vacuum system. The total recovery of solids and liquids was 95% (6.2096 g). The liquid portion was analyzed by quantitative gas chromatography. Methyl *tert*-butyl ether (4) was observed in 41% yield. The solid products (1.7989 g) were dissolved in water and titrated with standard HCl (14.5 ml of 1.00 *N* HCl). This represented 14.5 mequiv of base from the solid products.

Reaction of Bromo Acetal 7 with Potassium *tert*-Butoxide.—A Parr reaction bomb was charged with 1.1256 g (0.0101 mol) of potassium *tert*-butoxide, 6.4422 g (0.0871 mol) of *tert*-butyl alcohol, and 0.8623 g (0.0051 mol) of 7. The reactor was heated at 120 ± 0.1° for 8 hr. The final pressure reading was 30 psig. The reactor was cooled to room temperature and vented. The product mixture was transferred on a high vacuum system and the liquid products were collected in a cooled (−60°) receiver at 0.1 mm pressures. The liquid portion was analyzed by quantitative gas chromatography. The yield of ketene dimethyl acetal (6) was 52%. The total recovery of solid and liquid was 8.1359 g (97% recovery). No 4 was observed.

Registry No.—**1,** 24332-20-5; **2,** 7062-96-6; **3,** 7062-97-7; **4,** 1634-04-4; **6,** 922-69-0; **7,** 7252-83-7; potassium *tert*-butoxide, 865-47-4; *tert*-butyl alcohol, 75-65-0.

A Convenient Synthesis of Adamantylideneadamantane[1]

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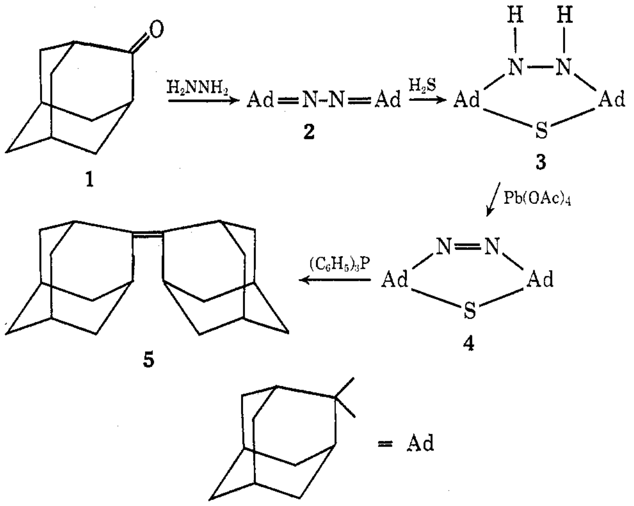
Recent investigations in this laboratory of the photooxidation of adamantylideneadamantane (5) in pinacolone solvent have provided the first direct evidence for the intermediacy of perepoxides in the addition of singlet oxygen to alkenes to form 1,2-dioxetanes.[2] Adamantylideneadamantane (5) has also been the subject of considerable interest because of the unusual stability of the 1,2-dioxetane[3] and the bromonium ion[4] obtained from this alkene.

We have found the synthesis of 5[5] *via* the carbenoid dimerization with *gem*-dibromoadamantane and zinc–copper couple to be very sensitive to the surface area and activity of the Zn-Cu couple. Reduction of the dibromide to adamantane is often the predominant reaction. We are therefore prompted to report a convenient, high-yield synthesis of 5 based on the extrusion of nitrogen and sulfur from an azo sulfide 4.[6]

Condensation of adamantanone (1) with hydrazine hydrate gives the azine 2. Addition of hydrogen sulfide to 2 yields the thiadiazolidine 3. Oxidation of 3 with lead tetraacetate affords the thiadiazine 4. Adamantylideneadamantane (5) is obtained by heating a melt of 4 and triphenylphosphine at 125°. The overall yield of 5 from 1 is 65%.



Experimental Section

Methods.—Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. The infrared spectra were measured on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model T-60 spectrometer with tetramethylsilane as internal standard. Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind.

Adamantanone Azine (2).—A solution of hydrazine hydrate (98%, 1.30 g, 26 mmol) in 15 ml of *tert*-butyl alcohol was added dropwise under nitrogen over a period of 45 min to a stirred refluxing solution of adamantanone (5.22 g, 35 mmol) in 60 ml of *tert*-butyl alcohol. After the addition was complete, the solution was refluxed for an additional 12 hr and subsequently allowed to stand at ambient temperature for 24 hr. The solvent was removed on a rotary evaporator to give an off-white crystalline mass to which was added 200 ml of water. The aqueous mixture was extracted with ether (4 × 100 ml). The combined ether extracts were washed with brine, dried ($MgSO_4$), and concentrated to give following recrystallization from hexane 5.10 g (98%) of 2: mp 313–315°; ir (KBr) 2885, 1622, and 1430 cm^{-1}; nmr ($CDCl_3$) δ 3.28 (m, 1 H), 2.62 (m, 1 H) and 1.93 (m, 12 H).

Anal. Calcd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.54. Found: C, 80.86; H, 9.51; N, 9.30.

Adamantanespiro-2′-(1′,3′,4′-thiadiazolidine)-5′-spiroadamantane (3).—Hydrogen sulfide was bubbled through a solution of the azine 2 (12.2 g, 41.1 mmol), and 5 mg of *p*-toluenesulfonic acid in 300 ml of 1:3 acetone–benzene at ambient temperature. Thin layer chromatography (silica gel, ethyl ether) indicated complete consumption of 2 after 12 hr. The solvent was removed on a rotary evaporator to give 12.8 g (95%) of the thiadiazolidine 3. This material was used in the subsequent step without further purification. Recrystallization from hexane afforded colorless crystals of 3: mp 300–307° dec; ir (KBr) 2880, 1705, and 1620 cm^{-1}; nmr ($CDCl_3$) δ 3.62 (br, 1 H) and 2.25–1.26 (m, 14 H).

2′,5′-Dihydroadamantanespiro-2′-(1′,3′,4′-thiadiazine)-5′-spiroadamantane (4).—To a suspension of $CaCO_3$ (20.7 g, 0.21 mol) in 300 ml of benzene at 0° was added in several portions lead tetraacetate (20.7 g, 46.7 mmol); the mixture was stirred for 20 min. A mixture of thiadiazolidine 3 (11.85 g, 35.9 mmol) and 300 ml of benzene was added dropwise with stirring over a period of 1.5 hr. After the addition was complete, the mixture was stirred at ambient temperature for 8 hr. Thin layer chromatography (silica gel, ether) indicated complete consumption of 3. Upon addition of 400 ml of water, a brown precipitate formed which was removed by filtration. The aqueous layer was separated, saturated with NaCl, and extracted with ether. The organic portions were combined, washed with brine, dried ($MgSO_4$), and concentrated to give 10.94 g (94%) of a yellow residue 4, mp 140–145°. This material was used in the subsequent step

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without further purification. Column chromatography over silica gel with 70:30 ether–hexane afforded colorless crystals of **4**: mp 145–146° dec; ir (KBr) 2870, 1710, 1570, and 1440 cm^{-1}; nmr ($CDCl_3$) δ 2.98 (m, 1 H), 2.78 (m, 1 H), and 1.95 (m, 12 H).

Anal. Calcd for $C_{20}H_{28}N_2S$: C, 73.12; H, 8.59. Found: C, 73.06; H, 8.98.

Adamantylideneadamantane (5).—An intimate mixture of thiadiazine **4** (1.092 g, 3.32 mmol) and triphenylphosphine (2.04 g, 7.79 mmol) was heated at 125–130° for 12 hr under an atmosphere of nitrogen. Column chromatography of the residue over silica gel with hexane gave 0.668 g (74%) of **5**, mp 184–185° (lit.[5] mp 184–187°).

Registry No.—**1**, 700-58-3; **2**, 39555-34-5; **3**, 40682-51-7; **4**, 40682-52-8; **5**, 30541-56-1; hydrazine, 302-01-2.

Reduction of *meso*-1,2-Dibromo-1,2-diphenylethane to 1,2-Diphenylethane by Hydrazine

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Many reagents dehalogenate vicinal dihalides to yield alkenes:[1] I^-, SH^-, ArS^-, $ArSO_2^-$, AlH_4^-, $RCHCOR^-$, $ArNH_2$, $ArNHNH_2$, C_5H_5N, Ar_2Hg, $(CH_3O)_3P$, Ar_3P, Zn, Mg, Cr(II), Bu_3SnH, Cl^-, Br^-, $Ph_2CCH_3^-$, Ph_2CH^-, $C_{10}H_8\cdot^-$, $RCHCO_2CH_3^-$, $(CH_3O)_3BH^-$, 2-$C_{10}H_7OH$, $(Me_3Si)_2Hg$, $(C_2H_5O)_3P$, Cu, Cu(I), Sn(II), Co(II), Fe(II), and Ti(III). These reactions all involve attack on halogen, leading either to an E2 transition state or a halonium ion intermediate (two-electron reductants) or to radical intermediates (one-electron reductants).[1k,l]

On the other hand only a single, inadvertent instance (below) of reduction to the *alkane* has been reported in systems of this type.[2] (The reduction of vicinal dibromide to alkane by $NaBH_4$ is apparently a pair of independent displacements by hydride.[3])

We have found that hydrazine reduces *meso*-stilbene dibromide ($STBr_2$) to bibenzyl (BB).

Results and Discussion

The Reaction with Hydrazine Alone.—Variable quantities of *cis*-1-bromo-1,2-diphenylethene are produced (Table I). The anti stereochemistry and the increasing proportion of this product (Table II) accompanying increasing concentration of N_2H_4 (a good base, $pK_a^{BH^+}$ 8.11) are consistent with straightforward E2 dehydrobromination of $STBr_2$ (eq 1). The

$$\underset{\text{meso}}{PhCHBrCHBrPh} + N_2H_4 \longrightarrow \underset{\text{cis}}{PhCH{=}CBrPh} + N_2H_5^+Br^- \quad (1)$$

more basic solvents also dehydrobrominate $STBr_2$ in parallel with N_2H_4 (Table I).

TABLE I

PRODUCTS[a] FROM *meso*-STILBENE DIBROMIDE[b] AND HYDRAZINE[c]

Solvent	Temp, °C	% BB	% ST	% *cis*-stilbene	% *cis*-α-Bromostilbene
$(CH_2OH)_2$	110	33	24		24
CH_3OH	65	39	27	Trace	28
$(CH_3)_2CHOH$	83	38	22	Trace	25
CH_3COOH	120	18	22		
$(CH_3)_2SO$	110	18	7		66
$HCON(CH_3)_2$	110	Trace	4		56
CH_3CN	80	6	10		79
1,4-Dioxane	101	7	8		87
Pyridine	116	4	6		85

[a] Time, 24 hr. [b] 0.2 *M*. [c] 4.2 *M*.

TABLE II

PRODUCT DEPENDENCE ON HYDRAZINE CONCENTRATION[a]

N_2H_4 molarity	Mol N_2H_4/mol $STBr_2$	% BB	% ST	% *cis*-α-Bromostilbene
21	105	8 ± 1	26 ± 1	72 ± 1
4.2	21	38 ± 2	22 ± 2	25 ± 2
0.84	4.1	56 ± 2	26 ± 1	4 ± 1

[a] In refluxing 2-propanol under N_2; $STBr_2$ concentration, 0.2 *M*. Results are mean values for 2–3 runs.

trans-Stilbene (ST) formation (Table I) results from stereospecific anti dehalogenation, implying nucleophilic attack on bromine by a two-electron donor,[11] either N_2H_4, the Br^- present as a result of reaction 1, or solvent. The production of BB as well as ST can then be rationalized by paths 2–4 or 5–7. Both paths

$$N_2H_4 + {>}CBrCBr{<} = {>}C{=}C{<} + NH_2\overset{+}{N}H_2Br\ Br^- \quad (2)$$

$$NH_2\overset{+}{N}H_2Br\ Br^- + 2N_2H_4 = NH{=}NH + 2NH_2\overset{+}{N}H_3\ Br^- \quad (3)$$

$$NH{=}NH + {>}C{=}C{<} = {>}CHCH{<} + N_2 \quad (4)$$

$$Br^- \text{ (or S)} + {>}CBrCBr{<} = {>}C{=}C{<} + Br_2 \text{ (or } BrS^+ + Br^-\text{)} \quad (5)$$

$$Br_2 \text{ (or } BrS^+ + Br^-\text{)} + 3N_2H_4 = NH{=}NH + 2N_2H_5^+Br^- \quad (6)$$

$$NH{=}NH + {>}C{=}C{<} = {>}CHCH{<} + N_2 \quad (7)$$

involve the potentially interceptible intermediate diimide, NH=NH. We demonstrated the presence of NH=NH by the reduction of cyclohexene added to the $STBr_2$–N_2H_4 reaction; cyclohexane is formed at the expense of BB (Table III).

TABLE III

EFFECT OF ADDED CYCLOHEXENE[a]

Additive	% BB	% ST	% *cis*-α-Bromostilbene	% C_6H_{12}
None	38 ± 2	22 ± 2	25 ± 2	
C_6H_{10}	17 ± 1	39 ± 1	43 ± 1	17 ± 1

[a] Equimolar C_6H_{10} and $STBr_2$ in refluxing 2-propanol; mol of N_2H_4:mol of $STBr_2$ = 21; time, 24 hr.

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