

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 $\text{C}_{20}\text{H}_{28}\text{N}_2\text{S}$: 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 , $\text{C}_5\text{H}_5\text{N}$, Ar_2Hg , $(\text{CH}_3\text{O})_3\text{P}$, Ar_3P , Zn , Mg , Cr(II) , Bu_3SnH , Cl^- , Br^- , $\text{Ph}_2\text{CCH}_3^-$, Ph_2CH^- , $\text{C}_{10}\text{H}_8^-$, $\text{RCHCO}_2\text{CH}_3^-$, $(\text{CH}_3\text{O})_3\text{BH}^-$, $2\text{-C}_{10}\text{H}_7\text{OH}$, $(\text{Me}_3\text{Si})_2\text{Hg}$, $(\text{C}_2\text{H}_5\text{O})_3\text{P}$, 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-diphenylethane are produced (Table I). The anti stereochemistry and the increasing proportion of this product (Table II) ac-

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TABLE I

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

Solvent	Temp, °C	% BB	% ST	% <i>cis</i> -stilbene	% <i>cis</i> - α -Bromo-stilbene
$(\text{CH}_2\text{OH})_2$	110	33	24		24
CH_3OH	65	39	27	Trace	28
$(\text{CH}_3)_2\text{CHOH}$	83	38	22	Trace	25
CH_3COOH	120	18	22		
$(\text{CH}_3)_2\text{SO}$	110	18	7		66
$\text{HCON}(\text{CH}_3)_2$	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.

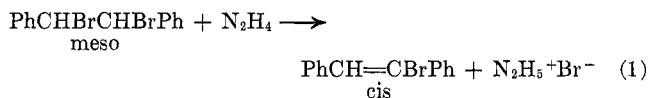
TABLE II

PRODUCT DEPENDENCE ON HYDRAZINE CONCENTRATION^a

N_2H_4 molarity	Mol N_2H_4 / mol STBr_2	% BB	% ST	% <i>cis</i> - α -Bromo-stilbene
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

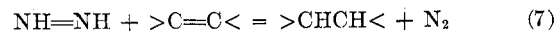
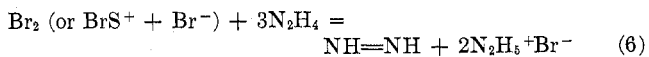
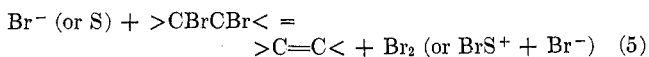
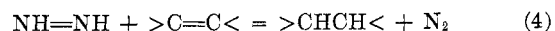
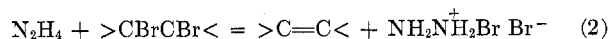
^a In refluxing 2-propanol under N_2 ; STBr_2 concentration, 0.2 M. Results are mean values for 2–3 runs.

companying increasing concentration of N_2H_4 (a good base, $\text{p}K_a^{\text{BH}^+}$ 8.11) are consistent with straightforward E2 dehydrobromination of STBr_2 (eq 1). The



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

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



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

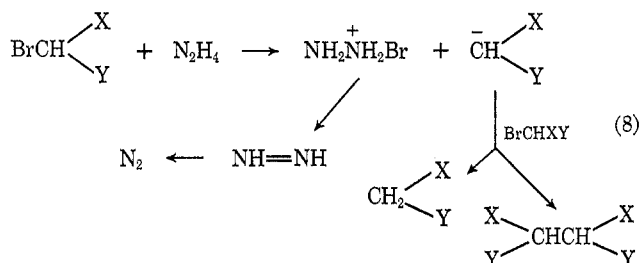
TABLE III

EFFECT OF ADDED CYCLOHEXENE^a

Additive	% BB	% ST	% <i>cis</i> - α -Bromo-stilbene	% C_6H_{10}
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.

Consider the choice between paths 2-4 and 5-7. Analogies for the former path are provided by nucleophilic displacements by N_2H_4 on bromine in the systems $BrCHXY$ ($X, Y = COOR, COR, CN, NO_2$) according to eq 8,⁴ by the demonstrated intermediacy



of diimide in the oxidation of hydrazine by CCl_4 ⁵ and by the protodebromination of hexabromobenzene.⁶ With respect to the second path, debromination by Br^- (eq 5) is known (at least in aprotic solvents; see below); the oxidation of N_2H_4 by halogen (eq 6) is rapid,⁷ and by analogy with oxidation by *N*-chloramines is expected to give diimide;⁸ the reduction of alkenes by diimide (eq 11) is well known. Thus both paths appear plausible and several tests can be designed to distinguish between them. If N_2H_4 is the nucleophile (as well as the dehydrohalogenating base in eq 1) then the ratio (BB + ST): α -bromostilbene should be independent of the hydrazine concentration. If Br^- or solvent is the nucleophile this ratio should decrease with increasing N_2H_4 concentration. Table II shows that a 25-fold increase in N_2H_4 concentration produces a *ca.* 44-fold depression, favoring path 5-7. Addition of Br^- increases (BB + ST) at the expense of dehydrobromination (below) in a 2-propanol solvent, which further implies that eq 5 is operative. The more nucleophilic solvents may dominate Br^- in eq 5, however. The above indications of dehalogenation by Br^- in 2-propanol contrast with the report that Br^- , though reactive in DMF, is unreactive toward $STBr_2$ in methanol (conditions unspecified).⁹ The explanation may be that the unreactivity derives from an unfavorable equilibrium position and is overcome in the present system by the reduction of product Br_2 (eq 6).

An excess of diimide is generally employed in alkene reductions in order to achieve good yields in the face of competitive disproportionation of diimide. Based on the behavior of similar systems, the 1:1 $NH=NH$ /ST ratio characteristic of the present system should result in a *ca.* 25% yield of BB.⁸ Reduction of ST with 1.0 molar equiv of $I_2 + N_2H_4$ gives in fact only 4% of BB. In contrast, the $STBr_2-N_2H_4$ reaction gives reduction yields [100 BB/(BB + ST)] as high as 84%. That the increased efficiency is not due to consumption of $NH=NH$ in the original solvent cage is shown by two pieces of evidence. (1)

Added cyclohexene is able to compete for the diimide. (2) The BB/ST ratio increases from *ca.* 0.2 to 2 during the reaction, *i.e.*, the efficiency of ST reduction increases with increasing ST concentration, implying that $NH=NH$ survives long enough to encounter ST diffusing up from bulk solution. The efficient BB formation thus appears to result from generation of $NH=NH$ at high dilution, favoring reduction of alkene over second-order disproportionation of diimide.

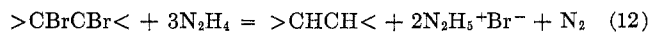
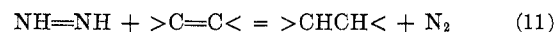
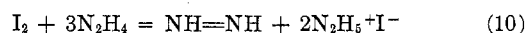
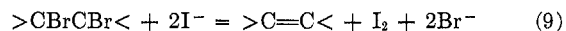
The Effect of Added Nucleophiles.—An added nucleophile, X^- , which is more reactive in dehalogenation than Br^- or N_2H_4 should increase (BB + ST) at the expense of α -bromostilbene. If the oxidized form, XBr , is also capable of oxidizing N_2H_4 rapidly, BB formation should be maintained, though perhaps in altered proportions. Table IV contains results for several nucleophiles.

TABLE IV
PRODUCTS FROM *meso*-STILBENE DIBROMIDE,
HYDRAZINE, AND ADDITIVES^a

Additive ^b	Mol N_2H_4 mol $STBr_2$	% BB	% ST	% <i>cis</i> - α -Bromo- stilbene
None	4.2	56	26	4
None ^c	21.0	39	27	28
KI	4.2	70	13	Trace
KI ^c	21.0	55	29	9
KBr	21.0	Trace	70	Trace
KBr ^c	21.0	37	42	16
NaSCN	4.2	57	24	9
NaSCN	6.0	65	25	5
$C_2H_5SO_2Na$	4.2	27	17	20
$C_2H_5SO_2Na$	6.0	30	20	21
$C_6H_5SK^d$	4.2	24	67	0
$C_6H_5SK^d$	6.0	21	68	0
KNCO ^d	4.2	19	14	38
KNCO ^d	6.0	22	16	50
KCN	4.2	6	7	28
KCN	6.0	4	9	29
$NaOCH_3$	4.2	10	18	80
$NaOCH_3$	6.0	10	21	67
Zn ^e	21	13	81	0
Ag ^{e,f}	21	32	64	0
None ^f	21	5	13	71
Cu(I) ^{f,g}	21	9	83	0

^a Solvent 2-propanol, except as noted. Reaction time 24 hr, at reflux in nitrogen atmosphere. ^b 0.2 M. ^c In CH_3OH . ^d Additional, unidentified peak in gas chromatogram. ^e From $AgNO_3$ in the presence of excess N_2H_4 . ^f In CH_3CN . ^g From $CuCl_2$ in the presence of excess N_2H_4 .

I^- , which is known to be a superior dehalogenating nucleophile, when added at low N_2H_4 concentration eliminates dehydrohalogenation altogether. The reaction is visualized as eq 9 + 10 + 11 = 12.¹⁰ The



BB/ST ratio is also increased. The other highly polarizable nucleophiles (SCN^- and PhS^-) increase

(10) The possible involvement of $PhCHI-CHBrPh$ is apparently eliminated by evidence that I^- attacks $STBr_2$ more rapidly at Br than at C, both in methanol and DMF.^{11,12}

(11) C. S. T. Lee, I. M. Mathai, and S. I. Miller, *J. Amer. Chem. Soc.*, **92**, 4602 (1970).

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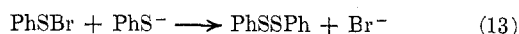
(6) I. Collins and H. Suschitzky, *J. Chem. Soc. C*, 2337 (1969). See also J. F. Bunnett and R. R. Victor, *J. Amer. Chem. Soc.*, **90**, 810 (1968).

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(9) W. K. Kwok, I. M. Mathai, and S. I. Miller, *J. Org. Chem.*, **35**, 3420 (1970).

(BB + ST) and depress α -bromostilbene strongly, as expected for attack on bromine.¹³ In the case of PhS⁻ the BB/ST ratio is also depressed, apparently owing to reaction 13 (known¹⁴ to accompany dehalo-

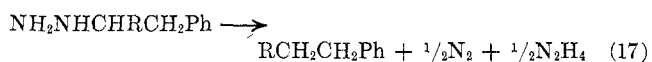
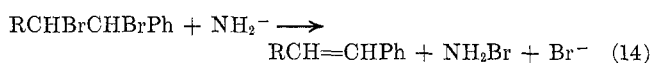


genation by PhS⁻) which competes with oxidation of N₂H₄.

The more basic nucleophiles attack H, and the proportion of α -bromostilbene increases.

The remaining dehalogenating agents [Zn, Ag, and Cu(I)] are efficient at suppressing dehydrobromination and generally depress the BB/ST ratio as expected for one-electron reductants, since their oxidized states do not oxidize hydrazine to diimide.¹⁵

Davis and Ansari,² attempting to dehydrobrominate RCHBrCHBrPh with NH₂⁻ in liquid ammonia, observed the formation of RCH=CHPh and RCH₂-CH₂Ph (ca. 2:1), which they attribute to eq 14-17.¹⁶



Our results open the possibility that diimide is also an intermediate in this reaction, production of hydrazine in eq 15 being followed by either reactions 2-4 or 5-7.

Other Substrates.—In preliminary experiments we failed to observe reduction of 1,2-dibromoheptane, *trans*-1,2-dibromocyclohexane, or 2,3-dibromopropanol by N₂H₄ under the conditions applied to STBr₂. This is consistent with the reported formation of only products of nucleophilic displacement on carbon in the reaction of 1,2-dihaloethanes with hydrazine.¹⁷

Experimental Section

General.—*cis*-1-Bromo-1,2-diphenylethane was prepared by the method of Wislicenus and Seeler¹⁸ and purified by trapping a center cut from the gas chromatographic peak. The ¹H nmr spectrum (CCl₄) displayed a broad singlet (δ 7.4 ppm) due to one phenyl group and the α proton, and a multiplet (δ 7.0 ppm) due to the other phenyl group, with area ratio 6:5.

Anal. Calcd for C₁₄H₁₁Br: C, 64.89; H, 4.28; Br, 30.83. Found: C, 64.68; H, 4.30; Br, 31.09.

meso-1,2-Dibromo-1,2-diphenylethane (Aldrich) was recrystallized from xylene: mp 237-238° (lit.¹⁹ mp 240-241°). Bibenzyl (Distillation Products Industries) was recrystallized from ethanol: mp 51.4° (lit.²⁰ mp 51.8°). All other chemicals were the highest quality commercial materials, used without purification.

Nmr spectra were obtained with a Varian A-60 instrument. Melting points were measured by hot-stage microscopy, and are corrected. Analyses were performed by Galbraith Laboratories, Inc.

Analytical Procedure.—Product solutions (containing 100 mg

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(17) R. F. Evans, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 4023 (1963).

(18) J. Wislicenus and F. Seeler, *Ber.*, **23**, 2693 (1895).

(19) W. K. Kwok and S. I. Miller, *J. Org. Chem.*, **35**, 4034 (1970).

(20) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

of diphenylacetylene per 25 ml as an internal standard) were gas chromatographed at 150° through 5-ft columns of 3% SE-30 on Varapost 30, 100/120 mesh, using a Varian Aerograph 600-D chromatograph with flame ionization detection. The sample size was 0.4-0.6 μ l; the carrier gas was N₂. For those runs to which cyclohexene was added the stationary phase was 12% Carbowax 1500 on Chromosorb W, 60/80 mesh, at 50°, and ethylbenzene was the internal standard. Response coefficients were determined on standard solutions and peak areas were measured by planimetry. Analyses were carried out in duplicate; precision ca. 3%. The precision of typical duplicate runs (standard deviation) is shown in Table II.

Reaction of Hydrazine with *meso*-Stilbene Dibromide.—340 mg (1.0 mmol) of STBr₂ and 4.0 ml of solvent were placed in a one-piece glass apparatus consisting of round-bottom flask, condenser, and port with Teflon stopcock (this apparatus served as a separatory funnel for the work-up, avoiding transfer of the contents). The condenser was capped with a mercury bubbler and oxygen was purged with a stream of nitrogen while the solution was heated to reflux (or 105° for solvents with bp >105°) for 5 min. The hydrazine and any additives were added through the condenser and the mixture was heated with magnetic stirring under nitrogen, usually for 24 hr. To the cooled mixture were added 7 ml of CHCl₃ and at least 25 ml of water. The aqueous layer was extracted twice more with 6-7 ml of CHCl₃ and the combined extracts were made up to 25.0 ml. This solution was dried by adding a few pieces of molecular sieve. In the runs to which cyclohexene was added toluene was used as extracting solvent.

The identity of bibenzyl was confirmed by isolation. We experienced difficulty with the liquid chromatographic separation of bibenzyl and *trans*-stilbene and resorted to destruction of the latter by aqueous permanganate. The product of a 1.0-mmol run in presence of KI, so treated, gave on elution from silicic acid with benzene-hexane (1:2) 0.128 g (0.70 mmol, 70%) of colorless crystals, melting point and mixture melting point identical with those of bibenzyl.

Extent of Reduction of Stilbene Due to Adventitious Oxidation of Hydrazine.—A solution of 180 mg (1.00 mmol) of *trans*-stilbene, 0.7 ml (21 mmol) of hydrazine, and 119 mg (1.00 mmol) of KBr in 4.0 ml of 2-propanol was refluxed for 24 hr under N₂. Work-up and analysis as above gave the following results for duplicate runs: bibenzyl, 3 and <1%; *trans*-stilbene, 100 and 97.8%.

Reduction of *trans*-Stilbene by Diimide Generated from N₂H₄ and I₂.—To a refluxing solution of 180 mg (1.00 mmol) of *trans*-stilbene and 0.35 ml (10 mmol) of hydrazine in 7 ml of methanol was added 254 mg (1.00 mmol) of iodine in 10 ml of methanol and the solution was refluxed for 35 min. Work-up and analysis as above revealed the presence of 0.038 mmol (3.8%) of bibenzyl and 0.930 mmol (93%) of *trans*-stilbene.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—*meso*-1,2-Dibromo-1,2-diphenylethane, 13440-24-9; 1,2-diphenylethane, 103-29-7; hydrazine, 302-01-2; *cis*-1-bromo-1,2-diphenylethane, 15022-93-2.

Di(phenyl-*d*₅)cyclopropenone¹

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In the young chemistry of the triafulvenes,² a leading role has been played by diphenylcyclopropenone

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(2) B. S. Thyagarajan, *Intra-Sci. Chem. Rep.*, **4**, 1 (1970).