(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 (known[14] to accompany dehalogenation by PhS^-) which competes with oxidation of N_2H_4.

$$PhSBr + PhS^- \longrightarrow PhSSPh + Br^- \qquad (13)$$

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 NH_2^- in liquid ammonia, observed the formation of RCH=CHPh and RCH_2CH_2Ph (*ca.* 2:1), which they attribute to eq 14–17.[16]

$$RCHBrCHBrPh + NH_2^- \longrightarrow RCH{=}CHPh + NH_2Br + Br^- \qquad (14)$$

$$NH_2Br + 2NH_2^- \longrightarrow NH_2NH^- + NH_3 + Br^- \qquad (15)$$

$$NH_2NH^- + RCH{=}CHPh + NH_3 \longrightarrow NH_2NHCHRCH_2Ph + NH_2^- \qquad (16)$$

$$NH_2NHCHRCH_2Ph \longrightarrow RCH_2CH_2Ph + {}^1/_2N_2 + {}^1/_2N_2H_4 \qquad (17)$$

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 N_2H_4 under the conditions applied to $STBr_2$. 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-diphenylethene was prepared by the method of Wislicenus and Seeler[18] and purified by trapping a center cut from the gas chromatographic peak. The ^1H nmr spectrum (CCl_4) 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 $C_{14}H_{11}Br$: 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 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 μl; the carrier gas was N_2. 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 $STBr_2$ 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 $CHCl_3$ and at least 25 ml of water. The aqueous layer was extracted twice more with 6–7 ml of $CHCl_3$ 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 N_2. 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 N_2H_4 and I_2.—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.

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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-diphenylethene, 15022-93-2.

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Di(phenyl-d_5)cyclopropenone[1]

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

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[1] Fulvenes and Thermochromic Ethylenes. Part 80. For part 79, see M. Rabinovitz and A. Gazit, *Tetrahedron Lett.*, 3523 (1972).

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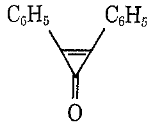
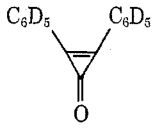
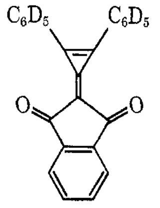
(**1**),[3,4] the readily available prototype of the "aromatic" [3]annulenone series. During a study of the electron impact behavior of triafulvenes derived from **1**,[5] it was deemed necessary to prepare di(phenyl-d_5)-cyclopropenone (**2**). We wish to report a straightforward synthesis of **2** and its application in the preparation of a deuterated triapentafulvalenequinone and di(phenyl-d_5)acetylene.



1



2



3

$C_6D_5C{\equiv}CC_6D_5$

4

Of the numerous methods available for the synthesis of **1**, the electrophilic substitution of aromatic substrates by trichlorocyclopropenium salts (the method of Tobey and West[6]) seemed promising. Indeed, treatment of trichlorocyclopropenium tetrachloroaluminate with benzene-d_6 in carbon disulfide solution[7] afforded the desired **2** in 70% yield. The structure of **2** was established by the elemental analysis and spectroscopic observations. The infrared spectrum of **2** showed characteristic cyclopropenone frequencies at 1840 and 1615 cm^{-1},[8] a C–D stretching absorption at 2240 cm^{-1}, and C–D out-of-plane bending bands at 560 and 540 cm^{-1} (five adjacent phenyl deuterium atoms). No absorption appeared in the pmr spectrum. The strongest signal in the mass spectrum of **2** (rel intensity 100%) was due to $[C_{14}D_{10}]\cdot^+$ ($[M - CO]\cdot^+$, *m/e* 188), while the intensity of the molecular ion at *m/e* 216 was only 0.4%. No signals appeared at *m/e* 178 and 206, ruling out the presence of **1** as a significant impurity. The relatively high abundance (6.1%) of the $[M - CO]^{2+}$ signal (at *m/e* 99) is noteworthy.

The use of **2** as a starting material for the synthesis of deuterated 1,2-diphenyltriafulvenes may be illustrated in the preparation of 1,2-di(phenyl-d_5)-4,5-benzotriapentafulvalene-3,6-quinone (**3**). Condensation of **2** with 1,3-indandione in boiling acetic anhydride in the presence of boron trifluoride etherate[9] gave **3** in 64% yield. The properties of **3** closely resemble those of its undeuterated analog.[10] The infrared spectrum of **3** shows a C–D stretching absorption at 2040 cm^{-1}, characteristic triafulvene frequencies at 1840 and 1485 cm^{-1}, a carbonyl stretching absorption at 1655 cm^{-1}, and a C–H and C–D out-of-plane bending band at 730 and 550 cm^{-1}, respectively. The pmr spectrum of **3** (in $CDBr_3$) exhibited only the symmetrical AA′BB′ pattern of the indandione protons centered at 7.85 (2 H, ortho to CO) and 7.65 ppm (2 H, meta to CO). The structure of **3** was confirmed by the molecular ion at *m/e* 344 in the mass spectrum and the absence of any signal in the region *m/e* 334–340.[5]

Finally, the photolytic decarbonylation of **2** in 2-propanol solution proceeded smoothly, providing a simple and efficient synthesis of di(phenyl-d_5)acetylene (**4**).[11,12] The molecular ion at *m/e* 188 was the strongest signal in the mass spectrum of **4**, while the signals due to undeuterated and partially deuterated diphenylacetylene at the *m/e* 176–182 region were completely absent. The facile synthesis of **4** may lead to practical syntheses of deuterated compounds derived from **4**, *e. g.*, phenanthrene-d_{10}.

Experimental Section

Melting points were taken on a Unimelt Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in Nujol and in KBr disks. Ultraviolet spectra were recorded on a Unicam Model SP800 spectrophotometer. Nmr spectra were taken on a Varian HA-100 spectrometer (TMS as internal standard). Mass spectra were measured on a Varian MAT CH-5 instrument operating at 70 eV, employing the direct insertion technique. Tetrachlorocyclopropene was obtained from Aldrich Chemical Co., Inc.

Di(phenyl-d_5)cyclopropenone (2).—A solution of 2.0 g (11 mmol) of tetrachlorocyclopropene in 2.5 ml of carbon disulfide was added dropwise, at 5°, under anhydrous conditions to a magnetically stirred suspension of 2.80 g (21 mmol) of anhydrous aluminum chloride in 6 ml of carbon disulfide and left for 15 min at room temperature. The resulting mixture containing trichlorocyclopropenium tetrachloroaluminate was treated dropwise with a solution of 5 ml of benzene-d_6 in 5 ml of carbon disulfide. After 16 hr at room temperature, the dark red complex was diluted with 200 ml of methylene chloride, cooled to 0°, and poured into 200 ml of hydrochloric acid (2 *N*). The organic fraction was washed with water, dried over magnesium sulfate, and evaporated to dryness under vacuum. Recrystallization of the remaining solid from cyclohexane gave 1.44 g (70% yield) of **2** as colorless needles: mp 119–120°; uv max (cyclohexane) 222 nm (log ϵ 4.24), 229 (4.23), 284 s (4.20), 291 (4.27), 300 (4.32), 316 (4.10), and 363 (3.00).

Anal. Calcd for $C_{15}D_{10}O$: C, 83.3; D, 9.3. Found: C, 83.2; D, 9.4.

1,2-Di(phenyl-d_5)-4,5-benzotriapentafulvalene-3,6-quinone (3).—A solution of 1.08 g (5 mmol) of **2** and 0.73 g (5 mmol) of 1,3-indandione in 30 ml of freshly distilled acetic anhydride containing 1 drop of boron trifluoride etherate was refluxed with magnetic stirring under anhydrous conditions for 2.5 hr and left at room temperature for 16 hr. The slightly red crystalline precipitate was filtered off and washed with methanol to give 1.1 g (64%) of crude **3**. Recrystallization from benzene afforded **3** as pale yellowish needles: mp 226°; uv max (CH_3CN) 232 nm (log ϵ 4.64), 250 s (4.46), 265 s (4.20), 287 (4.02), 297 (4.28), and 342 (4.66).

Anal. Calcd for $C_{24}D_{10}H_4O_2$: C, 83.7; D + H, 7.0. Found: C, 83.9; D + H, 7.1.

Di(phenyl-d_5)acetylene (4).—A solution of 0.108 g (0.5 mmol) of **2** in 200 ml of 2-propanol was irradiated for 2 hr at room temperature under argon with a 70-W uv lamp. Removal of the solvent *in vacuo* yielded **4**, mp 57° (0.085 g, 90%). Sublimation at 45–65° (0.6 mm) afforded **4** as colorless crystals, mp 59°.

Anal. Calcd for $C_{14}D_{10}$: C, 89.4; D, 10.6. Found: C, 89.5; D, 11.0.

Registry No.—**2,** 40736-43-4; **3,** 40682-48-2; **4,** 19339-46-9; tetrachlorocyclopropene, 6262-42-6; benzene-d_6, 1076-43-3; 1,3-indandione, 606-23-5.

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