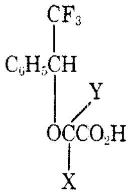
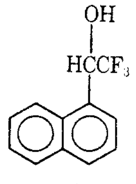
was found to be highly insoluble. Fractional crystallization is easily accomplished from ethyl acetate, after which the resolved alkoxy acid **2** can be efficiently converted into optically pure **1** by treatment with N-bromosuccinimide and subsequent hydrolysis of the resulting α-bromo ethers **4a–c**.[6] This scheme has also



4a, X = H; Y = Br
b, X = Br; Y = H
c, X = Y = Br



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been successfully applied to the resolution of 2,2,2-trifluoro-(1-napthyl)ethanol (**5**) and appears attractive for the resolution of other similar alcohols where conventional methods might be expected to fail.

Experimental Section[7]

dl-**2,2,2-Trifluorophenylethanol** (**1**) was prepared in 84% crude yield by the action of methanolic sodium borohydride on trifluoroacetophenone.[8]

2,2,2-Trifluorophenylethoxyacetic Acid (**2**).—To a solution of 92 g of crude **1** (containing *ca.* 23% bromobenzene) in 100 ml of ether was added excess cut sodium at a rate sufficient to maintain gentle reflux. After *ca.* 1.5 hr, alkoxide formation appeared to be complete, whereupon unreacted sodium was removed, 82 g of ethyl bromoacetate was cautiously added, and the mixture was heated to reflux for 2.5 hr. Hydrolysis to the alkoxy acid was accomplished by the addition of 450 ml of 10% sodium hydroxide and heating (steam bath) for 1 hr. The pH was adjusted to 9 by the addition of Dry Ice and the solution was extracted with ether to remove unreacted **1** (*ca.* 10%) and bromobenzene. The aqueous solution was acidified to pH 1 and extracted with ether, yielding the crude acid which was crystallized from 1 l. of petroleum ether (bp 90–120°) to give 68.7 g, mp 105.5–106°. The yield of **2** is 85% based on the amount of unrecovered **1**: ^{1}H nmr (acetone-d_6) δ 4.17 (2 H, AB quartet, $\Delta\nu_{AB} = 7.2$ Hz, $J_{AB} = 16.5$ Hz), 5.15 (1 H, quartet, $J = 6.8$ Hz), 7.45 (5 H, aromatic), and 8.80 ppm (1 H, COOH); ^{19}F nmr (CCl_4) δ 78.2 (doublet, $J = 6.8$ Hz).

Anal. Calcd for $C_{10}H_9F_3O_3$: C, 51.24; H, 3.87. Found: C, 51.49; H, 4.02.

Resolution of 2 with Amphetamine (**3**).—To a mixture of 56.5 g (0.24 mol) of unrecrystallized **2** (mp 102–104°) and 32.6 g (0.24 mol) of (−)-amphetamine (Aldrich Chemical Co.) was added 200 ml of hot ethyl acetate. The mixture was briefly heated on the steam bath to dissolve all solid, then allowed to stand at room temperature. After 4 hr, the resultant fluffy needles were collected by filtration and washed with cold ethyl acetate to give 22.7 g of salt, mp 149–153°. Two recrystallizations of this material using 12–14 ml of hot ethyl acetate per gram of salt gave 19.4 g (44% of theory) of material which did not change its properties upon further recrystallization: mp 155–156°; $[\alpha]^{25}\mathrm{D}$ −70.2 ± 1° (*c* 3.22, absolute ethanol).

Anal. Calcd for $C_{19}H_{22}F_3NO_3$: C, 61.78; H, 6.00; N, 3.80. Found: C, 61.65; H, 5.89; N, 3.66.

Concentration of the first crop mother liquors to 150 ml afforded a second crop of crystals, mp 128–130° (16.0 g), which did not significantly change its melting point or rotation upon successive recrystallization from ethyl acetate. This salt is not the other diastereomer but is a mixture of the two diastereomers and is richest in the salt of (+)-**2**.[9] The remaining mother liquors were concentrated at reduced pressure to remove ethyl acetate and then treated with 150 ml of 6 *N* hydrochloric acid to afford, after work-up, 32.7 g (0.14 mol) of partially resolved **2**. Treatment of this material with 18.9 g (0.14 mol) of (+)-**3** in 275 ml of ethyl acetate gave 16.0 g of material, mp 151–154°, which, after one recrystallization, afforded 13.4 g of salt melting at 155–156°; $[\alpha]^{25}\mathrm{D}$ +69.7 ± 1° (*c* 3.30, absolute ethanol). Purified (+)-amphetamine salt was converted into (+)-**2** with hydrochloric acid, yielding, after work-up, material melting at 87.5–88.5°, $[\alpha]^{24}\mathrm{D}$ +120 ± 1° (*c* 3.4 absolute ethanol).

Anal. Calcd for $C_{10}H_9F_3O_3$: C, 51.24; H, 3.87. Found: C, 51.31; H, 3.81.

Conversion of 2,2,2-Trifluorophenylethoxyacetic Acid (**2**) **into 2,2,2-Trifluorophenylethanol** (**1**).—To a solution of 11.5 g (0.05 mol) of (−)-**2** in 100 ml of carbon tetrachloride was added 13.2 g (0.07 mol) of N-bromosuccinimide and the mixture was heated to reflux on the steam bath while being irradiated with a GE sunlamp. After 4 hr, the ^{19}F nmr spectrum of an aliquot showed a trace of starting material and three major doublets 77.22, 77.56, and 77.60 ppm upfield of internal $CFCl_3$, tentatively assigned to the two diastereomeric monobromides **4a** and **b** and the α,α-dibromo derivative, **4c**. The solvent was evaporated, the residue was treated with 100 ml of 10% potassium hydroxide, and active alcohol **1** was collected by steam distillation. The distillate (250 ml) was extracted with ether, dried ($MgSO_4$), and concentrated. Molecular distillation of the residue (2 torr, 40°, cold finger at 0°) gave 6.88 g (80%) of (−)-**1**, identified by its ir and nmr spectra: $\alpha^{25}\mathrm{D}$ −40.8° (neat, $l = 1$) (lit.[2] $\alpha^{25}\mathrm{D}$ −41.18° (neat, $l = 1$). An nmr determination[10] of the optical purity of this carbinol failed to detect the presence of the (+)-enantiomer of **1**.

Registry No.—(+)-**1**, 340-05-6; (−)-amphetamine salt of **2**, 18521-88-5; (+)-**2**, 18521-89-6; (+)-amphetamine salt of **2**, 18521-90-9.

Acknowledgment.—This work was supported by Grant No. GM 14518 from the U. S. Public Health Service and by a U. S. Public Health Service Traineeship to T. G. B.

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[6] Crawford has reported the resolution of 1-trifluoromethylethanol *via* the adduct arising from condensation of the alcohol with acrylic acid. Hydrolysis is effected with base by means of the reverse Michael addition [J. W. C. Crawford, *J. Chem. Soc.*, 4280 (1965); *ibid.*, *C*, 2332 (1967)].

[7] Melting points were determined on a Büchi apparatus and are uncorrected. The nmr spectra were determined with a Varian A-56/60 spectrometer and chemical shifts are reported in δ units (parts per million downfield from internal tetramethylsilane or upfield from internal fluorotrichloromethane). Microanalyses were performed by J. Nemeth and his associates.

[8] The trifluoroacetophenone used in this work (Columbia Organic Chemicals, Columbia, S. C.) was shown by glpc to contain 23% bromobenzene. Reported crude yields are corrected for the bromobenzene present.

[9] As a consequence of the formation of this mixture, it is advisable to liberate the partially resolved acid **2** from the mother liquors of the initial crystallization and to proceed with the resolution of this material using the other enantiomer of amphetamine.

[10] (a) W. H. Pirkle, *J. Amer. Chem. Soc.*, **88**, 1837 (1966); (b) W. H. Pirkle and S. D. Beare, *ibid.*, **89**, 5485 (1967).

The Photolysis of Stilbene in the Presence of 2,3-Dihydropyran

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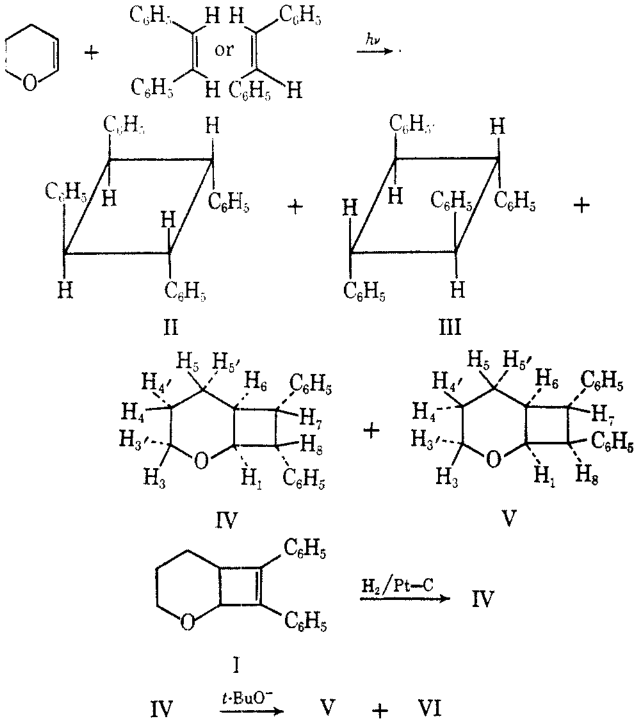
In an earlier paper we reported the photocycloaddition of diphenylacetylene to 2,3-dihydropyran to form

7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (I).[1] In order to observe the behavior of aryl olefins under similar reaction conditions we photolyzed solutions of *cis*-stilbene and *trans*-stilbene in the presence of 2,3-dihydropyran. The reaction mixtures were irradiated at 2537 Å for 48 hr while exposed to the atmosphere. At the end of this period the stilbene had reacted completely as indicated by glpc analysis. Four products were produced whose yields were virtually independent of stilbene isomer reactant. Two products were identified as *cis,trans,cis*-1,2,3,4-tetraphenylcyclobutane (II) and *trans,trans,trans*-1,2,3,4-tetraphenylcyclobutane[2] (III) (combined yields 24%). The other products were characterized as 7,8-*cis*-*exo*-diphenyl-2-oxabicyclo[4.2.0]octane (IV, 43%) and 7-*exo*-8-*endo*-diphenyl-2-oxabicyclo[4.2.0]octane (V, 23%) (Scheme I).

SCHEME I



The structural assignments of IV and V were supported by the following evidence. High resolution mass spectra established that both products were 1:1 adducts of stilbene and 2,3-dihydropyran. Catalytic hydrogenation (Pt–C) of I afforded one product whose glpc retention time and ir spectrum were identical with those of IV. Compound IV, on treatment with base, gave two products in approximately equal quantities having similar, but not identical, glpc retention times. One of these products (the one with slightly longer retention time) was found to have the identical retention time on two different columns as V. The other product (VI) was not isolated or characterized. These data indicate that IV is a *cis*-diphenylbicyclooctane and V is a *trans*-diphenyl isomer.

The stereochemistry was deduced from their nmr spectra, details of which are given in the Experimental Section. No coupling constants larger than 6.5 cps were found among the cyclobutane protons of IV. Since *cis* couplings for vicinal cyclobutane protons are frequently about 11 cps,[3] it appears unlikely that the cyclobutane protons have an all-*cis* configuration. In addition, the anomolously high chemical shift, *ca.* τ 6.7, for the bridgehead proton adjacent to oxygen (H_1) suggests shielding from the phenyl substituent *cis* to this proton. This is the expected product from the least sterically hindered transition state. We therefore assign the *cis*-*exo*-diphenyl structure to this compound.

The coupling constants (cycles per second) for the cyclobutane protons of V were found to be the following (approximate values): $J_{1,6} = 11$, $J_{1,8} = 10$, $J_{7,8} = 5$, $J_{6,7} = 3.5$. Spin-tickling experiments demonstrated couplings between all-vicinal protons assigned to the cyclobutane ring. The 7-*exo*-, 8 *endo*-diphenyl structure rests on the assumption that the couplings 10 and 11 cps reflect the *cis* vicinal configuration and the small couplings the *trans* configuration.

Solutions of *cis*- and *trans*-stilbene (0.1 *M*) in dihydropyran exposed to the atmosphere as well as under helium were irradiated in quartz vessels at 2537 Å. In the presence of oxygen the rates of stilbene isomerization were retarded but no corresponding changes in the rates of formation of IV and V were observed. The ratio of IV to V (1.87:1) remained constant throughout all reactions and was independent of the *cis*-stilbene:*trans*-stilbene ratio. Photolysis of a solution of *trans*-stilbene (0.01 *M*) in dihydropyran containing triphenylene (0.05 *M*) at 3500 Å provided evidence for sensitized isomerization of stilbene but no sensitized formation of IV and V.

These results preclude involvement of stilbene triplets in the formation of IV and V. The invariance of product ratio with respect to *cis*-stilbene:*trans*-stilbene ratio also precludes direct reaction of the first excited singlet states of stilbene if one assumes that such reactions are likely to be concerted.

We therefore conclude that formation of IV and V involves the vibrationally excited ground states reached through internal conversion from the first excited singlet states of stilbene. We cannot determine from our data whether these cyclization reactions occur in one or two steps.

Experimental Section

Melting points are uncorrected. Photolyses were conducted in a Rayonet photochemical reactor at 2537 or 3500 Å as indicated. The infrared spectra were obtained on a Beckman IR-4 spectrophotometer. High-resolution mass spectra were obtained on a CEC-21-110 instrument. Glpc was performed with a Barber Coleman Model 5000 gas chromatograph on 6-ft columns packed with 10% Apiezon L on Chromosorb W or 10% SE30 on Chromosorb W. Nmr spectra were taken on a Varian DP-60-IL instrument. The nmr spectra were too complex for accurate analysis. Approximate parameters were used to compute theoretical spectra by means of FREQINT IV[4] until satisfactory agreement was obtained between plots of theoretical spectra using a Calcomp plotter, and the appropriate portions of experimental spectra. The molecules were treated as five spin systems, utilizing parameters for H_1, H_5, H_6, H_7, and H_8.

Reaction of *cis* or *trans*-Stilbene with 3,4-Dihydropyran.—In

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[1] H. M. Rosenberg and P. Servé, *J. Org. Chem.*, **33**, 1653 (1968).

[2] See H. Schecter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, **85**, 1601 (1963), and references therein.

[3] I. Flemming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[4] A. A. Bothner-By and C. N-ar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961).

a quartz vessel a solution of stilbene, 7.5 g (0.03 mol), in 200 ml of 3,4-dihydropyran was irradiated at 2537 Å in a Rayonet photochemical reactor for 48 hr. After removal of the unreacted dihydropyran under reduced pressure, the crude reaction mixture was heated with petroleum ether and then cooled. A white crystalline product (2.45 g, 24% based on reacted stilbene) was isolated by filtration and characterized as a mixture of *cis,trans,-cis*-1,2,3,4-tetraphenylcyclobutane (II) and *trans,trans,trans*-1,2,3,4-tetraphenylcyclobutane (III): nmr ($CDCl_3$), τ 2.71, 2.91 (20 H, singlets, aromatic protons), 5.54, 6.33 (4 H, singlets, methine protons).[5] The filtrate was subjected to column chromatography on alumina (80–200 mesh). Elution with benzene–petroleum ether (bp 30–60°) (5:95) gave two products: 7,8-*cis-exo*-diphenyl-2-oxabicyclo[4.2.0]octane (IV) [3.65 g (43.3%); mp 48–50°; parent peak, 264.1495 ($C_{19}H_{20}O$); ir (thin film) 3040 (aromatic CH), 2900 (aliphatic CH), 1610, 1500 (aromatic C=C), 1053 (COC) and 740, 700 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) τ 2.75–2.83 (10 H, multiplet, aromatic protons), 5.75–5.87 (2 H, multiplet, H_7 and H_8), 6.13–6.38 (2 H, multiplet, H_3 and $H_{3'}$) 6.60–6.80 (1 H, multiplet, H_1), 7.10–7.35 (1 H, multiplet, H_6) and 8.36–8.70 (4 H, multiplet, H_4, $H_{4'}$, H_5 and $H_{5'}$), $J_{1-6} = 4.5$ cps, $J_{1-8} = 6.5$, $J_{6-7} = 6.5$, $J_{7-8} = 6.5$]; 7-*exo*,8-*endo*-diphenyl-2-oxabicyclo[4.2.0]octane (V) [1.92 g (23.6%); mp 36–38°; parent peak, 264.1525 ($C_{19}H_{20}O$); ir (thin film) 3030 (aromatic CH), 2890 (aliphatic CH), 1600, 1490 (aromatic C=C), 1110 (COC) and 750, 740, 700 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) τ 2.72–2.90 (10 H, aromatic protons), 5.7 (1 H, multiplet, H_7), 6.0 (1 H, multiplet, H_1), 6.6 (1 H, multiplet, H_8), 6.20–6.32 (2 H, multiplet, H_3, $H_{3'}$), 7.0 (1 H, multiplet, H_6) and 8.25–8.50 (4 H, multiplet, H_4, $H_{4'}$, H_5, $H_{5'}$), $J_{1,6} = 11$ cps, $J_{1,8} = 10$ cps, $J_{7,8} = 5$ cps, $J_{6,7} = 3.5$ cps].

The Hydrogenation of 7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (I).[1]—In a Paar hydrogenation vessel 0.2 g of 5% Pt on charcoal was added to a solution of I, 1.0 g in 35 ml of absolute ethanol. The solution was then subjected to hydrogenation at 50 lb pressure for 24 hr. The reaction mixture was filtered and evaporated to a volume of 10 ml. The solution was then analyzed by glpc. The chromatogram showed the presence of two peaks with areas in the ratio of 1:4. The retention time of the smaller peak was identical with that of I and the larger peak corresponded to IV. The solvent was removed under vacuum and the products were separated by column chromatography on alumina. The ir spectrum of the reduction product was identical with that of IV.

Isomerization of 7,8-*cis-exo*-Diphenyl-2-oxabicyclo[4.2.0]-octane (IV).—A mixture of 7,8-*cis-exo*-diphenyl-2-oxabicyclo-[4.2.0]octane 0.1 and 0.2 g of potassium *t*-butoxide in 25 ml of ethanol was refluxed for 12 hr. The solvent was evaporated under vacuum and the residue was taken up in ether which was than washed with water and dried over anhydrous $MgSO_4$. The ether solution was analyzed by glpc. The chromatogram showed two new peaks with approximately equal areas. The retention times of one of these components on two different columns was identical with those of V.

Registry No.—*cis*-Stilbene, 645-49-8; *trans*-stilbene, 103-30-0; 2,3-dihydropyran, 110-87-2; IV, 18521-18-1; V, 18521-19-2.

[5] Values reported in ref 2 are the following: τ 2.95 and 5.60 for II and 2.79 and 6.37 for III.

The Hydrogenolysis of Trithiocarbonates

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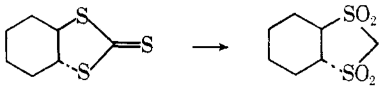
The hydrogenolysis of carbon–sulfur bonds has found extensive use in both structure determination and synthesis.[1] However, relatively little attention has been focused on the hydrogenolysis of trithiocarbonates. Gibson[2] reported an unsuccessful attempt to convert ethylene trithiocarbonate into 1,3-dithiolane, while McSweeney and Wiggins[3] reported the reductive desulfurization of the trithiocarbonate derivatives of carbohydrates with Raney nickel to the corresponding dideoxy compound. In 1960, Iqbab and Owen[4] found cyclic trithiocarbonates, upon treatment with lithium aluminum hydride, undergo smooth reductive fission to vicinal dithiols. More recently, Owen and coworkers[5,6] described the oxidation of *trans*-1,2-cyclohexane trithiocarbonate (I) with excess per acid in which the thiocarbonyl is converted into a methylene group affording the corresponding methylenedisulfonyl compound II. We now wish to report the results of our studies in which the direct catalytic hydrogenolysis of trithiocarbonates yield the corresponding 1,3 disulfides (see Table I).



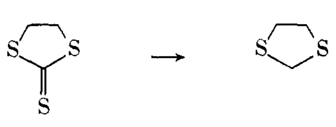
I II

TABLE I

CATALYTIC HYDROGENOLYSIS OF TRITHIOCARBONATES

	Reaction conditions		Product			
Trithio-carbonate	Time, hr	Temp, °C	1,3-Di-sulfide	Yield, %	Bp, °C (mm)	n_D
I	12	150	V	50	53–55 (0.01)	1.5706 (31°)
III	16	150	IV	88	75 (25)	1.5980 (23°)
VI	12	160	VII	12	70–72 (20)	1.5331 (21°)

Contrary to Gibson's observation[2] we have found hydrogenolysis (2000 psi) of ethylene trithiocarbonate (III) in benzene containing a catalytic amount of molybdenum trisulfide at 150° afforded 1,3-dithiolane (IV) as a colorless liquid in 88% yield. The infrared (1415 cm^{-1}) and pmr spectrum [δ 3.83 (singlet, 2 H, $-SCH_2S-$), 3.13 (singlet, 4 H, $-CH_2S-$)] are in complete agreement with IV; both spectra were identical with the spectra of an authentic sample[2] of IV. The reaction is clean with the only other product observed (*via* glpc) being ethylene dimercaptan in ~2% yield. Since current synthetic routes[7] to 1,3-dithiolane suffer from either low yield and/or polymer formation this method offers a



III IV

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[1] G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, **12**, 356 (1962); H. Hauptmann and W. F. Walter, *Chem. Rev.*, **62**, 347 (1962); R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965.

[2] D. T. Gibson, *J. Chem. Soc.*, 12 (1930).

[3] G. P. McSweeney and L. F. Wiggins, *Nature*, **168**, 874 (1951).

[4] S. M. Iqbab and L. N. Owen, *J. Chem. Soc.*, 1030 (1960).

[5] A. K. M. Anisuzzaman and L. N. Owen, *Chem. Commun.*, 16 (1966).

[6] T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc.*, 807 (1967).

[7] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1958.