sity of the C–D stretching frequency at 2190 cm^{-1} with that of an authentic sample. Since the infrared and nmr spectra of the *cis*-3-deuterio-*cis*-2-chlorobicyclo[3.1.0]hexane were virtually identical with those of an authentic sample, it was concluded that the addition of deuterium chloride was predominately *cis*.

The nmr spectrum of the deuterated *trans*-2 chloride shows a doublet (J = 4.3 cps) at τ 5.71 for the tertiary proton α to the chlorine atom, and thus the *trans*-2 chloride must be *trans*-3-deuterio-*trans*-2-chlorbicyclo[3.1.0]hexane. The infrared spectra of the *cis*-3-deuterio-*trans*-2 chloride and *trans*-3-deuterio-*trans*-2 chloride were different, with the *trans*-3-deuterio chloride exhibiting two unique, strong bands at 990 and 928 cm^{-1} and the *cis*-3-deuterio chloride showing a unique, strong band at 870 cm^{-1}. The absence of a band at 870 cm^{-1} in the infrared spectrum of the *trans*-3-deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane, from the deuterium chloride addition to bicyclo[3.1.0]hexene-2, demonstrates that less than 1% *trans* addition occurred. Nmr comparison of the deuterated *trans*-2 chloride addition product with undeuterated *trans*-2 chloride and with the *cis*-3-deuterio-*trans*-2 chloride demonstrated that the *trans*-3-deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane obtained was 95–100% deuterated.

***cis*-3-Deuterio-*cis*-2- and *cis*-3-Deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane.**—To a stirred solution of 0.93 g (7.9 mmoles) of *cis*-3-deuterio-*trans*-2-bicyclo[3.1.0]hexanol[4] (98–100% deuterated) and 7 drops of pyridine in 13 ml of ether was added 1.25 g (10.5 mmoles) of thionyl chloride. After the addition was completed, the reaction mixture was heated at reflux for 3 hr. The ether solution was decanted from the reaction flask leaving behind the pyridine hydrochloride. The ether and excess thionyl chloride were removed at reduced pressure, using a rotary evaporator, to yield 1.02 g (93%) of product. The mixture was shown to consist of 7% deuterated 4-chlorocyclohexene, 37% *cis*-3-deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane, and 56% *cis*-3-deuterio-*cis*-2-chlorobicyclo[3.1.0]hexane when analyzed as described in the hydrogen chloride addition to bicyclo[3.1.0]hexene-2.

The nmr spectrum of the *cis*-3-deuterio-*trans*-2-chlorobicyclo-[3.1.0]hexane shows a singlet (τ 5.71) for the proton α to the chlorine atom, a complex splitting pattern in the region τ 7.40 to 8.70 corresponding to two tertiary and three methylene protons, and a complex splitting pattern (τ 9.60 to 10.00) for the two methylene protons on the cyclopropane ring.

The nmr spectrum of the *cis*-3-deuterio-*cis*-2-chlorobicyclo-[3.1.0]hexane shows a complex splitting pattern (τ 5.38 to 5.73) for the proton α to the chlorine atom, a complex band (τ 7.50 to 8.80) for two tertiary and three methylene protons, and a complex pattern for the two methylene protons on the cyclopropane ring in the region τ 9.32 to 9.70.

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1,2-Diphenylcyclobutene

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Treatment of 1,4-dichloro-1,4-diphenylbutane (III) with sodium amide in liquid ammonia produced 1,2-diphenylcyclobutene (IV) in excellent yield. 1,2-Diphenylcyclobutene (IV) was easily reduced to *cis*-1,2-diphenylcyclobutane (V), which in turn was isomerized readily with potassium *t*-butoxide in dimethyl sulfoxide to *trans*-1,2-diphenylcyclobutane (VI). The stereochemistry of V and VI was assigned from their method of preparation and from their nmr spectra.

We have recently found that treatment of either *cis*- or *trans*-2,5-diphenyltetrahydrothiophene dioxide with ethylmagnesium bromide produced 1,2-diphenylcyclobutene (IV) in moderate yield. Consideration of the possible mechanisms of this reaction led us to believe that reaction of 1,4-dichloro-1,4-diphenylbutane (III) with sodium amide would also yield 1,2-diphenylcyclobutene (IV).[2] This seemed particularly probable in view of the synthesis of α,α'-dimethylstilbene from α-phenylethyl chloride and sodium amide by Hauser and co-workers.[3]

A mixture of *meso*- and *dl*-1,4-dichloro-1,4-diphenylbutane (III) was easily prepared from dibenzoylethane (I) by the reactions shown in the accompanying equations. Reduction of dibenzoylethane (I) with sodium borohydride gave, in excellent yield, only the low-melting isomer of 1,4-diphenyl-1,4-butanediol (II), mp 90.5–92°. This was converted into a mixture of *meso*- and *dl*-1,4-dichloro-1,4-diphenylbutane (III) with anhydrous hydrogen chloride in acetic acid. The mixture could be separated into the pure *meso* and *dl* isomers, mp 106–107.5 and 36.5–38.5°, respectively,[4] by crystallization from ethanol. However, for the preparation of 1,2-diphenylcyclobutene the crude mixture of isomers gave yields comparable with those from the pure isomers. (See Scheme I.)

Reaction of 1,4-dichloro-1,4-diphenylbutane (III) with sodium amide yielded 1,2-diphenylcyclobutene (IV) in 89% yield. The structure of IV was established by analysis, by comparison of its ultraviolet spectrum with that of related compounds,[5] from its nmr spectrum, and by oxidation to dibenzoylethane (I). The most intense peak in the mass spectrum of IV corresponded to the molecular ion (206) of IV or the molecular ion of 2,3-diphenylbutadiene. The physical properties of IV correspond very well with those subsequently reported for 1,2-diphenylcyclobutene synthesized by alternate methods.[2]

The formation of 1,2-diphenylcyclobutene (IV) from 1,4-dichloro-1,4-diphenylbutane (III) probably proceeds by an intramolecular S$_N$2 displacement reaction similar to that shown to occur during the for-

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[1] Taken from part of the Ph.D. thesis of A. G. Zielske, Aug 1966. This research was partially supported by the Petroleum Research Fund, American Chemical Society PRF-1090-A1.

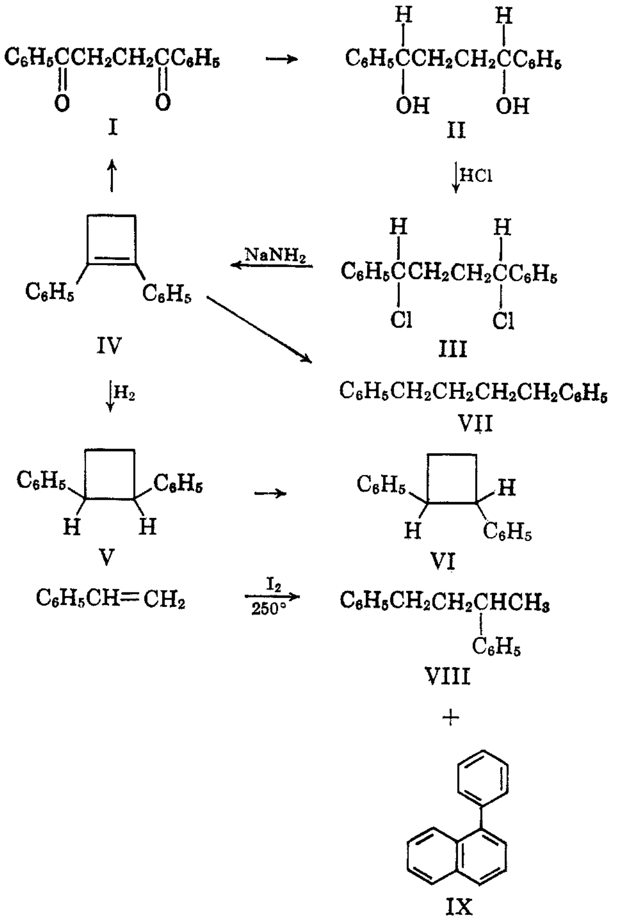
[2] (a) A preliminary report of this work has been published: R. M. Dodson and A. G. Zielske, *Chem. Commun.*, 353 (1965). Since our report, publications describing three different syntheses of 1,2-diphenylcyclobutene have appeared: (b) M. S. Newman and G. Kaugers, *J. Org. Chem.*, **30**, 3295 (1965); (c) E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 3937 (1965); (d) M. A. Battiste and M. E. Burns, *ibid.*, 523 (1966).

[3] W. R. Brasen, S. W. Kantor, P. S. Skell, and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 397 (1957).

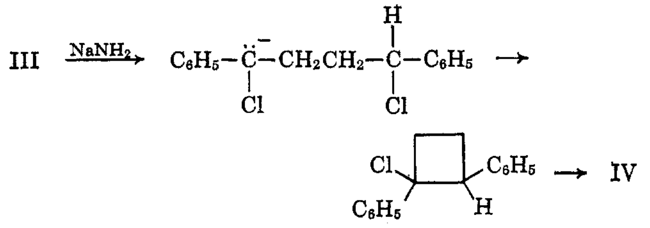
[4] The stereochemistry of *meso*-1,4-dichloro-1,4-diphenylbutane, mp 106–107.5°, and *dl*-1,4-dichloro-1,4-diphenylbutane, mp 36.5–38.5°, was assigned from the stereochemistry of the respective *cis*- and *trans*-2,5-diphenyltetrahydrothiophenes obtained from them on treatment with Na_2S. This work will be reported in a future publication.

[5] (a) K. Nagarajan, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 449 (1964); (b) A. T. Blomquist and E. A. LaLancette, *ibid.*, **83**, 1387 (1961); (c) R. Breslow, J. Lockhart, and A. Small, *ibid.*, **84**, 2793 (1962); (d) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

SCHEME I



mation of α,α′-dimethylstilbene from α-phenylethyl chloride.[3]



Reduction of 1,2-diphenylcyclobutene (IV) using either a platinum oxide or a palladium-on-carbon catalyst and limiting hydrogen uptake to 1 molar equiv gave *cis*-1,2-diphenylcyclobutane (V) in 83% yield. Hydrogenation in ethanol plus 1 drop of perchloric acid, using 10% palladium-on-carbon catalyst and allowing the reaction to proceed until hydrogen uptake had stopped, yielded 1,4-diphenylbutane (VII).

The *cis*-1,2-diphenylcyclobutane was readily isomerized to the *trans* isomer by treatment with potassium *t*-butoxide in dimethyl sulfoxide. Very little of the *cis* isomer (*ca.* 1%, vpc) remained after equilibration. The configurations of the *cis* and *trans* isomers were assigned from the methods of synthesis. The assignments were confirmed by the nmr spectra. The absorption band for the α protons of the *trans*-1,2-diphenylcyclobutane (VI) was centered at τ 6.45, while that of *cis*-1,2-diphenylcyclobutane was centered at 6.06. Increased shielding of the α protons by the phenyl groups would be expected in the *trans* isomer.[6] An attempt to prepare the *trans* isomer by reduction of 1,2-diphenylcyclobutene (IV) with lithium in liquid ammonia yielded only 1,4-diphenylbutane (VII).

Levina[7] and co-workers have reported the synthesis of a *cis–trans* mixture of 1,2-diphenylcyclobutane (7.3% yield) by the decomposition of 3,6-diphenyl-1,4,5,6-tetrahydropyridazine at 250–300° in the presence of potassium hydroxide and platinum. In order to determine the possibility of thermal isomerization of *cis*-1,2-diphenylcyclobutane and in order to provide some evidence for the composition of the 1,2-diphenylcyclobutane previously reported, *cis*-1,2-diphenylcyclobutane (V) was heated at 250° for 0.5 hr in a sealed, evaluated tube. Only styrene and *trans*-1,2-diphenylcyclobutane (9.7% yield) were isolated from this reaction. Vapor phase chromatography failed to show any *cis*-1,2-diphenylcyclobutane. The 1,2-diphenylcyclobutane synthesized by Levina, *et al.*,[7] should be almost entirely the *trans* isomer. A comparison of their reported refractive index ($n^{20}\text{D}$ 1.5822) with that of our *trans* isomer ($n^{20}\text{D}$ 1.5808) supports this conclusion.

The presence of 1,2-diphenylcyclobutane among the dimers formed by the thermal dimerization (polymerization) of styrene has been reported.[8] Since large quantities of styrene are formed during the thermal isomerization of *cis*-1,2-diphenylcyclobutane (V), the possibility exists than the *trans* isomer (VI) was formed largely from styrene and not by the direct isomerization of the *cis* isomer. Purified styrene was heated in a sealed tube under conditions identical with those used for the isomerization of *cis*-1,2-diphenylcyclobutane (V). Only traces of material were eluted from the vpc column in the region where one would expect the diphenylcyclobutanes. The *trans*-1,2-diphenylcyclobutane (VI) must be formed by the direct isomerization of the *cis* isomer.

In order to explore further the feasibility of the direct synthesis of *trans*-1,2-diphenylcyclobutane from styrene, purified styrene containing a small amount of iodine was heated in a sealed tube at 250° for 0.5 hr. Of the materials eluted in that portion of the gas chromatogram that would correspond to dimeric products, only 2.4% was eluted in a region even approximating that of *trans*-diphenylcyclobutane. The major products isolated were 1,3-diphenylbutane (66.3% of dimeric material) and 1-phenylnaphthalene (29.2% of dimeric material). No further attempts were made to identify the other dimeric products of the reaction (2.1 and 2.4%) or to prepare diphenylcyclobutane by this method.

Experimental Section[9]

1,2-Dibenzoylethane was prepared from *trans*-1,2-dibenzoylethylene by reduction with sodium hydrosulfite (yield 74–

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(6) (a) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961); (b) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958); (c) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 119 ff; (d) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965).

(7) R. Ya. Levina, Yu. S. Shabarov, M. G. Kuz'min, N. I. Vasil'ev, and E. G. Treschchova, *Dokl. Akad. Nauk SSSR*, **121**, 303 (1958); *Chem. Abstr.*, **53**, 13555*b* (1959).

(8) (a) K. F. Mueller, *Makromol. Chem.*, **79**, 128 (1964); (b) I. S. Bengelsdorf, *J. Org. Chem.*, **25**, 1468 (1960).

(9) All melting points were determined on a calibrated Fisher-Johns hot stage. The nmr spectra were taken with a Varian Associates Model A-60 spectrometer on 15% solutions in deuteriochloroform using 2% tetramethylsilane as an internal standard. Petroleum ether refers to that material of bp 60–68°.

96%)[10] or with stannous chloride[11] (yield 76%). For the preparation of large quantities of 1,2-dibenzoylethane, the stannous chloride reduction was preferred.

1,4-Diphenyl-1,4-butanediol.—Dibenzoylethane (50.0 g, 0.210 mole, mp 145.5–147°) in 1050 ml of ethanol was heated until solution was complete. Then sodium borohydride (7.95 g, 0.210 mole) in 100 ml of water was added rapidly to the hot solution. An additional 200 ml of water was added to clarify the solution. The reaction was heated under reflux for an additional 15 min. The solution was cooled to room temperature, cautiously acidified with 30 ml of glacial acetic acid in 70 ml of water, then evaporated under vacuum to 600 ml. The product was isolated by extraction with ether (400 ml). Crystallization of the product from chloroform–petroleum ether yielded 42.9 g (84.6% of theory) of 1,4-diphenyl-1,4-butanediol, mp 90.5–92° (lit.[13] mp 89–90°).

Reduction of 1,2-dibenzoylethane with lithium aluminum hydride[12] in tetrahydrofuran gave a mixture of isomers (quantitatively) from which 1,4-diphenyl-1,4-butanediol, mp 111–112°, could be obtained (32% yield) by crystallization from chloroform–petroleum ether. Smaller yields of the lower melting isomer could also be isolated.

1,4-Dichloro-1,4-diphenylbutane.—Dry, gaseous hydrogen chloride was bubbled slowly through a solution of 1,4-diphenyl-1,4-butanediol (44.0 g, 0.182 mole, mp 88–92°) in 900 ml of glacial acetic acid for 4.25 hr. The resulting solution was then allowed to stand for 21 hr. Thin layer chromatographic analysis of the reaction mixture showed that no diphenylbutanediol was present. Dry nitrogen was bubbled through the acetic acid solution to free it from excess hydrogen chloride. The solution was then concentrated under vacuum to approximately 100 ml. The product which separated during these processes (18 g, mp 94–103°) was collected by filtration. The acetic acid solution was diluted with 500 ml of water and the remaining product was isolated by ether extraction (29 g of mushy, yellow crystals). The over-all yield of crude material (47 g) was 93%.

Crystallization of the high-melting material from ethanol gave 15.0 g of *meso*-1,4-dichloro-1,4-diphenylbutane, mp 102.5–104°. The analytical sample melted at 106–107.5° (lit.[13] mp 103–104°).

Anal. Calcd for $C_{16}H_{16}Cl_2$: C, 68.83, H, 5.78; Cl, 25.40. Found: C, 68.48; H, 5.87; Cl, 25.14.

Fractional crystallization of the lower melting material from ethanol yielded 6.85 g of pure *dl*-1,4-diphenyl-1,4-dichlorobutane, mp 35–37°; the analytical sample had mp 36.5–38.5°.

Anal. Calcd for $C_{16}H_{16}Cl_2$: C, 68.83; H, 5.78; Cl, 25.40. Found: C, 68.73; H, 5.60; Cl, 25.49.

A similar mixture of the *dl*- and *meso*-1,4-dichloro-1,4-diphenylbutanes was obtained from either the high-melting or low-melting 1,4-diphenyl-1,4-butanediol.

1,2-Diphenylcyclobutene (IV).—Sodium metal (1.17 g 0.0510 g-atom) was dissolved in 250 ml of liquid ammonia to which a few crystals of ferric nitrate had been added. After the reaction of sodium was complete (15 min), a solution of 2.84 g (0.0102 mole) of 1,4-diphenyl-1,4-dichlorobutane (mixture of isomers) in 75 ml of anhydrous ether was added to the sodium amide solution over a period of 30 min. The reaction mixture was stirred for a total of 5.5 hr. Additional ether was added and the ammonia was allowed to evaporate overnight. Ethanol was added to the stirred suspension followed by aqueous acetic acid. The ether solution was then washed with water, 10% aqueous hydrochloric acid, then water, and was dried over magnesium sulfate. Analysis of this ether solution with thin layer chromatography indicated the absence of 1,4-diphenyl-1,4-dichlorobutane and the presence of only one product. The ether was evaporated. The residue (2.06 g, 0.010 mole, 98% yield, mp 43–49°) was chromatographed on 52 g of silica gel. Elution with petroleum ether yielded 1.86 g (89%) of 1,2-diphenylcyclobutene, mp 50–52°. Crystallization from ethanol gave analytically pure material: mp 51.5–52.5°; $\lambda_{max}^{ethanol}$ 227 mμ (ϵ 23,200), 297 mμ (ϵ 17,800); $\lambda_{sh}^{ethanol}$ 309 mμ (ϵ 16,800); nmr ($CDCl_3$) τ 2.33–2.95 (complex multiplet, 9.8 H); 7.27 (singlet, 4.2 H). The physical properties are in excellent agreement with those recently reported by others.[2b-d]

Anal.[14] Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.01; H, 6.80.

A similar reaction on a smaller scale starting with *meso*-1,4-diphenyl-1,4-dichlorobutane gave 1,2-diphenylcyclobutene in 69% yield.

1,2-Dibenzoylethane (I) from 1,2-Diphenylcyclobutene (IV).—A solution of 0.20 g of 1,2-diphenylcyclobutene (IV) in 30 ml of *t*-butyl alcohol was treated with 1.445 g of sodium metaperiodate and 0.23 g of potassium carbonate in 1.0 ml of water. To this was added, at room temperature, 14 ml of an aqueous, 0.4% potassium permanganate solution over a period of 23 hr. 1,2-Dibenzoylethane (I), mp and mmp 146.5–148.5° (30% yield), was isolated by dilution of the reaction mixture with water, extraction of the product with ether, and chromatography of the product on silica gel.

***cis*-1,2-Diphenylcyclobutane (V).**—Hydrogenation of 1,2-diphenylcyclobutene (IV) in ethanol using either a platinum oxide catalyst or a palladium-on-charcoal catalyst and limiting hydrogen uptake to 1 mole gave *cis*-1,2-diphenylcyclobutane: mp 38–39°; 83% yield from ethanol; nmr ($CDCl_3$) τ 3.05 (singlet, 10.1 H, phenyl groups), 5.88–6.21 (multiplet centered at 6.06, 1.8 H, α protons), 7.45–7.75 (multiplet centered at 7.62, 4.1 H, β protons).

Anal. Calcd for $C_{16}H_{16}$; C, 92.26; H, 7.74. Found: C, 92.35; H, 7.84.

***trans*-1,2-Diphenylcyclobutane (VI).**—A solution of 0.317 g of *cis*-1,2-diphenylcyclobutane and 0.20 g of potassium *t*-butoxide in 25 ml of anhydrous dimethyl sulfoxide was stirred at 75° for 22 hr. The reaction mixture was poured into water and extracted with benzene. Vapor phase chromatography of the benzene solution showed little, if any, material corresponding to the *cis*-1,2-diphenylcyclobutane (slightly raised base line, 43 cm from air peak, possibly 1%) and only one product, corresponding to the *trans*-1,2-diphenylcyclobutane (52 cm from the air peak). The oil obtained by evaporation of the benzene solution was purified by chromatography on silica gel and elution with petroleum ether. In this way 0.283 g (90% yield, $n^{20}D$ 1.5808) of pure *trans*-1,2-diphenylcyclobutane was obtained: ν_{max}^{neat} 692, 748, 1030, 1445, 1497, 1600, 2860, 2940, 2970, 3020, 3060, 3080 cm^{-1}; nmr ($CDCl_3$) τ 2.81 (singlet, 10.0 H, phenyl protons), 6.27–6.61 (multiplet centered at 6.45, 2.0 H, α protons), 7.52–8.05 (multiplet centered at 7.75, 4.0 H, β protons). Analysis of this material by vapor phase chromatography showed the presence of only one product.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.68.

Thermal Isomerization of *cis*-1,2-Diphenylcyclobutane (V).—*cis*-1,2-Diphenylcyclobutane (0.417 g, mp 38–39°) was divided equally into four Pyrex tubes (6-mm outside diameter, 6 in. in length). The tubes were evacuated, sealed, then submerged in a metal bath (250°) for 0.5 hr. The tubes were cooled and then opened, and their contents were dissolved in benzene and combined. Analysis of the benzene solution by vapor phase chromatography showed the presence of two products, one eluted at 1.6 from the air peak and the other at 52 cm from the air peak. The material eluted first was shown to be styrene. Its infrared spectrum, refractive index, and retention time on vapor phase chromatography were all identical with those of an authentic sample of styrene.

The benzene solution was evaporated and the residue was dissolved in petroleum ether. Chromatography of this material on silica gel gave 0.040 g (9.7% yield) of *trans*-1,2-diphenylcyclobutane. This material showed only one peak, 52 cm from the air peak, on vapor phase chromatography. Its infrared spectrum and nmr spectrum were identical with those of the *trans*-1,2-diphenylcyclobutane obtained from the base-catalyzed isomerization.

1,4-Diphenylbutane (VII) from 1,2-Diphenylcyclobutene (IV).—Lithium wire (0.10 g, 0.0145 g-atom) was added to a solution of 0.501 g (0.00243 mole) of 1,2-diphenylcyclobutene in 30 ml of anhydrous ether and 100 ml of liquid ammonia. The resulting deep red solution was stirred for 1.5 hr; then the excess lithium and the lithium amide were decomposed by the addition of 50 ml of ether–95% ethanol (1:1). The liquid ammonia was allowed to evaporate, the resulting solution was diluted with water, and the organic product was isolated by extraction. Crystallization of the product from 95% ethanol gave 1,4-diphenylbutane, mp

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[10] J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **45**, 1303 (1923).

[11] P. S. Bailey and R. E. Lutz, *ibid.*, **70**, 2412 (1948).

[12] R. E. Lutz and J. S. Gillespie, Jr., *ibid.*, **72**, 344, 2002 (1950).

[13] M. Protiva, M. Borovicha, and J. Pliml, *Collection Czech. Chem. Commun.*, **21**, 607 (1956); *Chem. Listy*, **49**, 1802 (1955); *Chem. Abstr.*, **50,** 9317*i* (1956).

[14] The analysis was run on a sample of 1,2-diphenylcyclobutene prepared from *trans*-2,5-diphenyltetrahydrothiophene 1,1-dioxide. It was identical in all respects (melting point, mixture melting point, infrared spectrum) with that described above.

50.5–51.5° (yield 73% of theory). The melting point of a mixture of this material with 1,2-diphenylcyclobutene was markedly depressed. The product was identical with an authentic sample of 1,4-diphenylbutane (melting point, mixture melting point, nmr.

1-Phenylnaphthalene (IX) and 1,3-Diphenylbutane (VIII) from Styrene.—Commercial styrene was washed with aqueous sodium hydroxide, water, then dried over sodium sulfate and distilled, bp 30–32° (10 mm). Iodine (0.030 g) was added to 15 ml of this material. The iodine–styrene solution was placed into four Pyrex glass tubes (6-mm outside diameter, 6 in. in length; 0.10 ml per tube). The tubes were cooled in liquid nitrogen, evacuated, sealed, and submerged in a metal bath (250°) for 0.5 hr. The tubes were cooled and then opened. Their contents were dissolved completely in benzene and combined. Vapor phase chromatography of the benzene solution showed the presence of four possible dimeric materials eluted at 30 (2.1%), 42 (66.3%), 58.5 (2.4%), and 101 cm (29.2%) from the air peak.

Material in the 42-cm peak was collected from the gas chromatographic column by condensation into a glass capillary tube. Its infrared and nmr spectra [($CDCl_3$) τ 2.80, 2.86 (10 H, phenyl groups), 7.08–7.70 (multiplet, 2.9 H, protons α to phenyl group), 7.87–8.36 (multiplet, 2.0 H, CH_2), 8.70 and 8.81 (doublet, 3.1 H, CH_3)] were identical with those of authentic 1,3-diphenylbutane.[15] Retention times of the two samples on gas chromatography were also identical.

The infrared spectrum of material corresponding to the 101-cm gas chromatographic peak was identical with the infrared spectrum of 1-phenylnaphthalene.[16] See Table I for vpc results.

TABLE I

VAPOR PHASE CHROMATOGRAPHIC RESULTS

Compound	Eluted, cm from air peak
1,2-Diphenylcyclobutene	32
cis-1,2-Diphenylcyclobutane	40
trans-1,2-Diphenylcyclobutane	52
1,4-Diphenylbutane	53
1,3-Diphenylbutane	42
1-Phenyltetralin	62
1-Phenylnaphthalene	101

Vapor Phase Chromatography.—The vapor phase chromatograms were run on an Aerograph gas chromatograph, Model A-90P. A 20% Apiezon L, 60–80 firebrick (5 ft × 0.25 in.) column was used throughout. Helium was used as the carrier gas at a pressure of 20 psi (91 ml/min). The chart speed was 1.7 cm/min. The following temperatures were used throughout: column, 200°; injector, 250°; collector, 220°; detector, 250°.

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(15) We are indebted to Dr. Herman Pines, Northwestern University, for a sample of 1,3-diphenylbutane.

(16) Sadtler Standard Spectra, No. 21084, The Sadtler Research Laboratories.

Bridged Ring Compounds. VIII.[1] 1-Halobicyclo[2.2.2]octanes

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Convenient syntheses of 1-chloro-, 1-bromo-, and 1-iodobicyclo[2.2.2]octanes are described. Reaction of 1-methoxybicyclo[2.2.2]octanes with acetyl halides in the presence of stannic chloride afforded 1-halobicyclo-[2.2.2]octanes in moderate yields. An analogous reaction of 4-methoxybicyclo[2.2.2]octan-2-ones with acetyl chloride afforded a mixture of 4-acetoxybicyclo[2.2.2]octan-2-ones and 4-chlorobicyclo[2.2.2]octan-2-ones. An acid-catalyzed reaction of 1-methoxybicyclo[2.2.2]octanes with acetic anhydride furnished 1-acetoxybicyclo-[2.2.2]octanes.

In recent years functionally substituted bridgehead structures have been of interest in study of the theoretical organic chemistry and, as a result, a number of bridged bicyclic compounds have been prepared. This paper deals with the convenient syntheses of 1-halobicyclo[2.2.2]octane derivatives which are potentially useful starting material[2] for the preparation of bridgehead-substituted derivatives.[3]

1-Chloro- and 1-bromobicyclo[2.2.2]octanes have been obtained by rather difficult and multistep syntheses. Three approches have been used for the syntheses: (1) halogenation of bicyclo[2.2.2]octan-1-ol[4] or bicyclo[2.2.1]heptane-1-methanol[5] with Lucas reagent, (2) the Hunsdiecker reaction of bicyclo[2.2.2]-octane-1-carboxylic acid,[6] and (3) free-radical attack at the bridgehead hydrogen atom of a bicyclic hydrocarbon.[7]

Recently 1-methoxybicyclo[2.2.2]octanone derivatives (**1**) have become readily available.[8] Wolff–Kishner reduction of **1** gave 1-methoxybicyclo[2.2.2]-octanes (**2**). Reaction of **2a**, **2b**, and **2c** each with acetyl chloride in the presence of stannic chloride at room temperature afforded 1-chlorobicyclo[2.2.2]octanes in higher than 80% yield. An analogous reaction of **2a** with acetyl bromide and with acetyl iodide furnished 1-bromobicyclo[2.2.2]octane (**4**) and 1-iodobicyclo[2.2.2]octane (**5**),[9] respectively.[10] Thus, 1-halobicyclooctanes can be prepared from methyl vinyl ketone and 2-methoxy-1,3-butadiene in four steps in an over-all yield of about 50%. The infrared and nmr spectra of the halogenated products are consistent with the assigned structures (*cf.* Table I). These spectra

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(1) Paper VII: K. Morita and Z. Suzuki, *Bull. Chem. Soc. Japan*, **39**, 1350 (1966).

(2) *Cf.* K. B. Wieberg and B. R. Lowry, *J. Am. Chem. Soc.*, **85**, 3188 (1963).

(3) For the syntheses of bridgehead-substituted bicyclo[2.2.2]octanes, see (a) K. Morita, *et al.*, *J. Org. Chem.*, **30**, 533 (1965); **31**, 229, 3106 (1966); (b) J. C. Kauer, R. E. Benson, and G. W. Parshall, *ibid.*, **30**, 1431 (1965), and literature cited therein; (c) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5183 (1964); (d) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(4) A. A. Sayingh, thesis, Columbia University Libraries, 1952.

(5) W. P. Whelan, Jr., thesis, Columbia University Libraries, 1952.

(6) F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963); see also ref 3d.

(7) A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

(8) K. Morita, M. Nishimura, and Z. Suzuki, *J. Org. Chem.*, **30**, 533 (1965); K. Morita and Z. Suzuki, *Tetrahedron Letters*, 263 (1964); K. Morita and T. Kobayashi, *J. Org. Chem.*, **31**, 229 (1966).

(9) An attempted preparation of iodobicyclooctane (**5**) by the Hunsdiecker reaction has been failed; *cf.* ref 6.

(10) Reaction of **2a** with acetyl fluoride in the presence of an acid catalyst afforded 1-fluorobicyclo[2.2.2]octane, mp, *ca.* 152° (most parts sublimes without melting). *Anal.* Calcd for $C_8H_{13}F$: F, 14.8; Found: 14.7. A detailed account of this interesting new fluorination reaction and its extention to other system will be reported shortly.