

tain and this might be the source of the large coupling constant.

As was mentioned previously, the chemical shift data presented in Table II vary over a wide range. The chemical shift of the protons of cyclopropane³ is downfield by 13.2 c.p.s. with respect to tetramethylsilane (at 60 Mc.) and for the cyclopropane derivatives listed in Table II the resonance positions of the ring protons are shifted to lower fields. Substituents which are magnetically anisotropic, such as a phenyl or a carbonyl group, have a marked effect on the chemical shifts. It is also possible that there is a ring-current effect on chemi-

cal shifts comparable to that in benzene but of considerably smaller magnitude. It is interesting to compare the ring proton chemical shifts in 1,1-dichloro-2-methoxycyclopropane to those in 1,1-dichloro-2-ethoxycyclopropane. The replacement of a methoxy group by an ethoxy group increases the shielding of the ring protons. It is rather surprising that the changes in shielding are essentially equal for all three ring protons. It may also be noted that the proton *cis* to the substituent in these two compounds is more shielded than the *trans* proton while in cyclopropane-1,1,2-tricarboxylic acid the *trans* proton is more shielded.

[CONTRIBUTION No. 2767 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

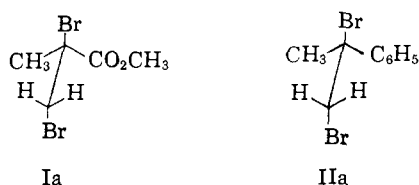
Nuclear Magnetic Resonance Spectroscopy. The Stereospecificity of the Long-range Spin-Spin Coupling in 1,2-Dibromo-2-phenylpropane¹

BY DONALD R. DAVIS AND JOHN D. ROBERTS

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The stereospecific long-range, proton-proton spin coupling in 1,2-dibromo-2-phenylpropane has been shown by deuterium labeling to probably be a *trans* interaction. New preparations of the *cis*- and *trans*- α -methyl- β -bromostyrenes and the lithium reagents corresponding thereto are described.

Previously² we reported a stereospecific long-range, proton-proton spin coupling in methyl α,β -dibromoisobutyrate (I), which substance appears to exist in a preferred conformation Ia,³ most likely that with the bromines *trans*. One of the non-equivalent³ methylene protons of I is coupled to the protons of the C-methyl group with



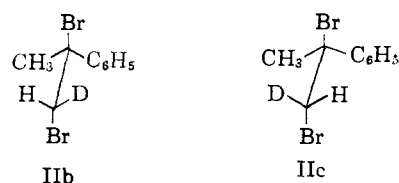
$J = 0.75$ c.p.s. It was not known whether the coupled proton is that which is *trans* or *gauche* to the methyl group.

An analogous long-range splitting of 0.65 c.p.s. has been observed (*cf.* Fig. 1A) in the spectrum of 1,2-dibromo-2-phenylpropane (here and later shown in the conformation IIa with the bromines *trans*; this is expected to be the *avored* conformation by analogy with 1,1-difluoro-1,2,2-tribromo-2-phenylethane).^{2,3} If the conformation is correctly assigned, then the spectra of the stereospecifically deuterium-labeled isomers IIb and IIc are only consistent with the long-range coupling involving the proton disposed *trans* to the methyl group. The evidence is deduced from the n.m.r. curves of Fig. 1 which shows the methylene resonances

(1) Supported in part by the Office of Naval Research and the Undergraduate Research Participation Program of the National Science Foundation.

(2) D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

(3) (a) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 3; (b) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4595 (1957).



of the following mixtures of IIa-IIc

Fig.	IIa, %	IIb, %	IIc, %
1A	100
1B	18	29	54
1C	36	43	21

Figure 1B shows the broad peak of the methylene proton of IIc located between the low-field pair of peaks of IIa. The smaller, broadened triplet of IIb is likewise in the expected position⁴ with respect to the high-field resonances of IIa. The weakly coupling deuterium nucleus, which possesses a spin of 1 and therefore has three equally probable orientations in a magnetic field, causes an adjacent proton to appear approximately as a triplet.⁵ Clearly, that proton of IIc, which is presumed to be *trans* to the methyl group, is the long-range coupled proton of IIa. The long-range coupling cannot easily be observed in the spectrum of IIc due to the additional small coupling (~ 1.5 c.p.s.) to the deuterium. Furthermore, as can be seen from methylene resonances of IIb, the lines due to the H-D coupling are broadened and distorted, almost surely by intermediate rates of magnetic relaxation arising from the interactions involving

(4) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1961, Chap. 2.

(5) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 10.

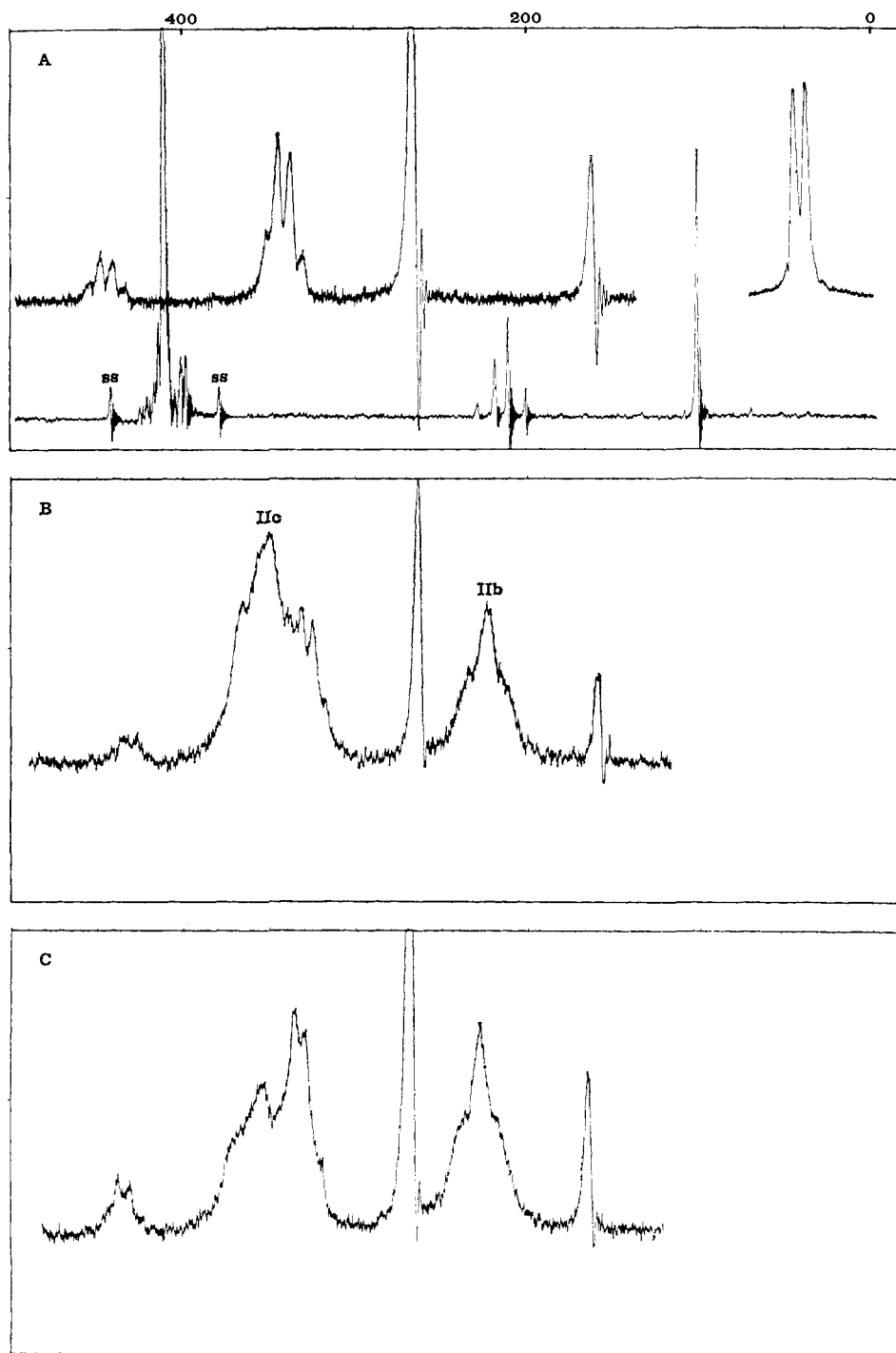


Fig. 1.—Nuclear magnetic resonance spectra at 60 Mc.: A, 1,2-dibromo-2-phenylpropane (IIa); the calibration is c.p.s. downfield from tetramethylsilane; the expanded inserts show the methylene and methyl resonances and were recorded so that the total chart width equals 50 c.p.s. B, Methylene protons of IIa containing the two 1-deuterio-1,2-dibromo-2-phenylpropanes (IIb and IIc), but predominantly IIc. C, methylene protons of a different mixture of IIa, IIb and IIc containing IIb as the principal deuterium-labeled form. The whole sweep of the curves B and C are on the same scale as the insert of A. The notation SS is for spinning sidebands.

the deuterium electric quadrupole moment.^{5,6} Figure 1C shows the spectrum of a mixture containing predominately IIb as the deuterated species. The relative areas of the low-field (long-range coupled) and high-field broad peaks confirms the

(6) Reference 3a, Chap. 5.

assignment made above of these peaks to, respectively, IIc and IIb.

Synthetic Procedures.—The stereospecifically deuterium-labeled 1,2-dibromo-2-phenylpropane isomers were prepared by addition of bromine to *cis*- and *trans*- α -methyl- β -deuteriostyrene (*cis*- and

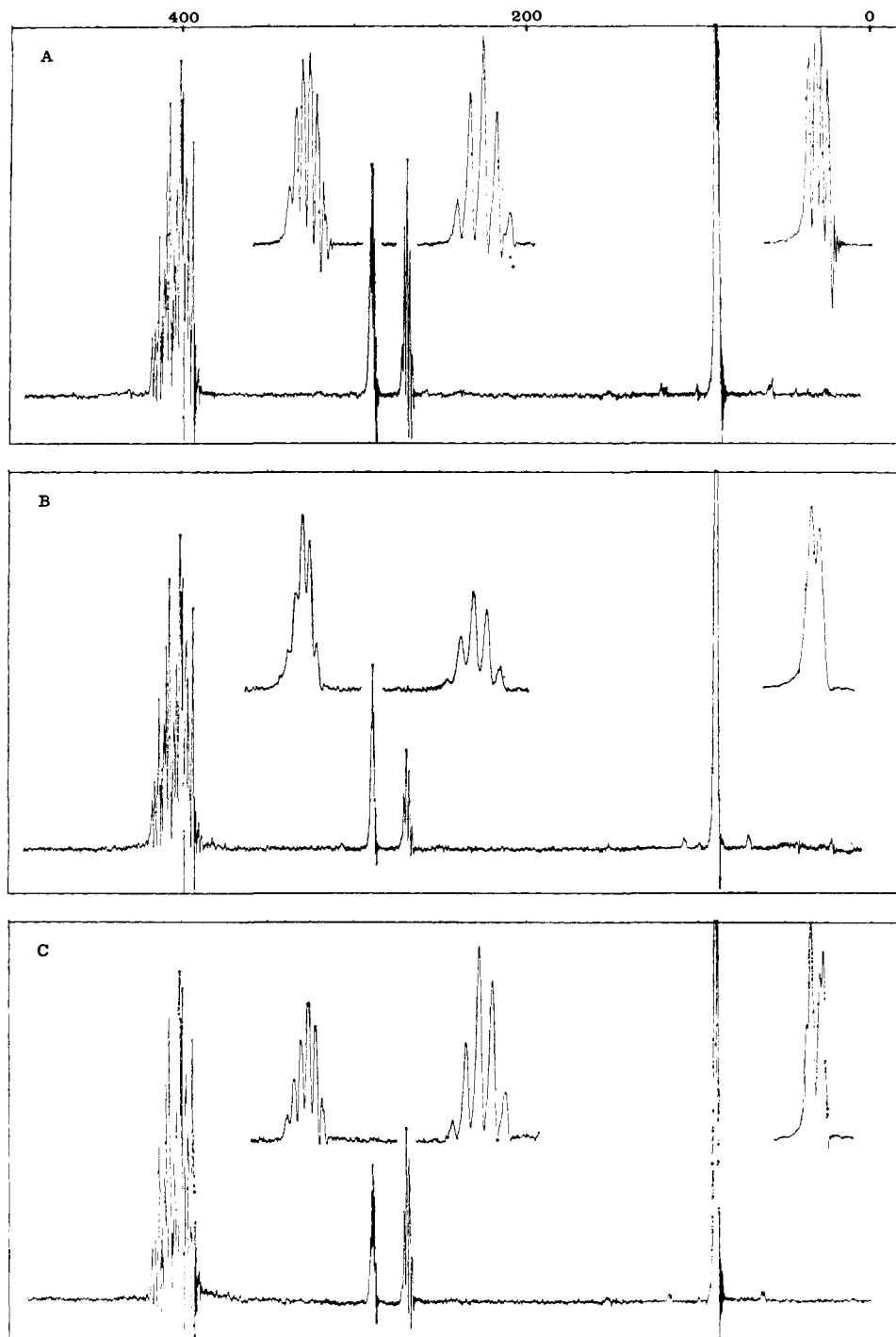


Fig. 2.—Nuclear magnetic resonance spectra at 60 Mc.; the calibration is c.p.s. downfield from tetramethylsilane; the expanded inserts of the vinyl and methyl resonances were recorded on a scale such that the total chart width equals 100 c.p.s.: A, α -methylstyrene (III); B, a mixture of III and *cis*- and *trans*- α -methyl- β -deuteriostyrene (*cis*- and *trans*-IIIa) containing predominantly *trans*-IIIa; and C, a mixture of III and IIIa in which *cis*-IIIa is the principal deuterium-labeled form.

trans-IIIa), respectively. The sequence for the *trans* isomer is shown below. The parallel sequence starting with *cis*- α -methyl- β -bromostyrene (*cis*-IV) yielded IIb.

trans- α -Methyl- β -bromostyrene (*trans*-IV) was prepared by elimination of hydrogen bromide from α -methylstyrene dibromide with sodium

methoxide. A small amount (3–6%) of *cis*-IV was also formed. A mixture containing 82% *cis*-IV was obtained by irradiation of *trans*-IV with a mercury arc in the presence of β -acetonaphthone as photosensitizer.⁷

(7) G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

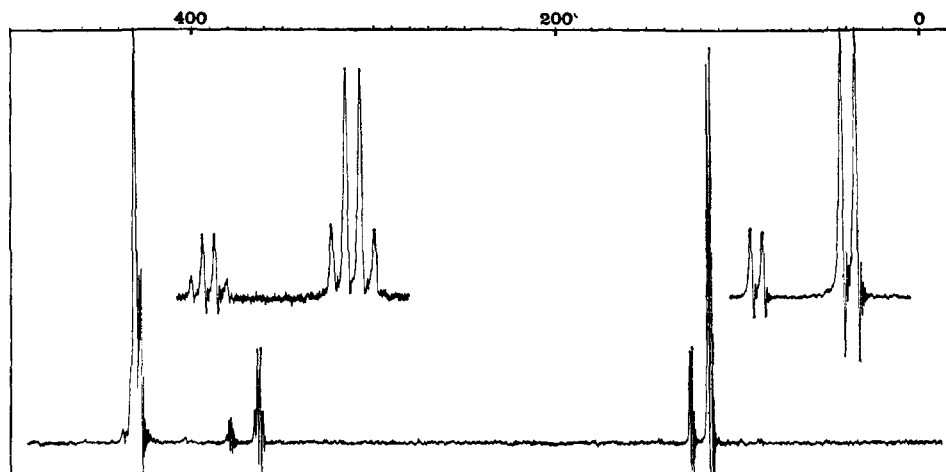
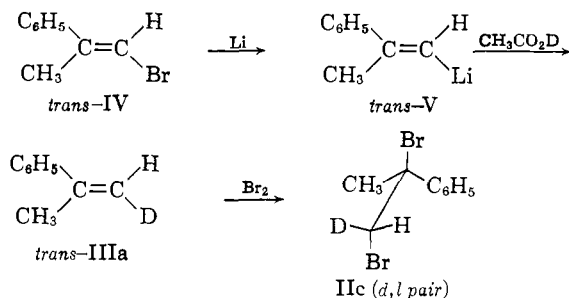


Fig. 3.—Nuclear magnetic resonance spectrum at 60 Mc. of *cis*- and *trans*- α -methyl- β -bromostyrene (IV). The mixture contained predominantly (82%) *cis*-IV. Calibration is c.p.s. downfield from tetramethylsilane. The expanded inserts of the vinyl and methyl resonances were recorded on a scale such that the total chart width represents 100 c.p.s.

Treatment of *cis*- and *trans*-IV with lithium metal^{8d} in ether solution for about 1 hr. at -30 to



-50° , followed by addition of deuterioacetic acid gave up to 65% yields of α -methylstyrene (III) and α -methyl- β -deuteriostyrene (IIIa). Despite precautions to maintain strictly anhydrous conditions for the reaction, the non-deuterated III generally comprised about 20–35% of the total product isolated. The deuteration was further complicated by failure to have complete retention of configuration in the over-all reaction, presumably as the result of *cis-trans* isomerization of the vinyl-lithium intermediate.⁸ For example, when virtually 100% *trans*-IV was carried through the reaction sequence, about 30–35% of the deuterium was found in the *cis* position. These results suggested that it might be desirable to treat the vinyl-lithium reagent (V) with an active deuterium compound as soon as possible after its formation. It was found feasible to “titrate” the bright red-brown vinyl-lithium derivative (V) with an ether solution of deuterioacetic acid concurrently with its generation from bromide and lithium wire. Even though the lifetime of V was thereby reduced to the order of a few seconds, the deuterium content and stereochemical distribution in the resulting *cis*- and *trans*- β -deuterio- α -methylstyrenes (IIIa) were not significantly changed from those

(8) (a) D. Y. Curtin and E. E. Harris, *J. Am. Chem. Soc.*, **73**, 2716 (1951); (b) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 4519 (1951); (c) D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *ibid.*, **77**, 4566 (1956); (d) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958).

resulting from the original procedure. The possibility that the product exchanged deuterium for hydrogen or was subsequently isomerized seems to be eliminated by the observation that a mixture of III and the *cis*- and *trans*-deuterio derivatives IIIa was not detectably affected by ten days at room temperature in an n.m.r. tube with an equal volume each of ether, acetic acid and water.

Electronic integration of peak areas of n.m.r. spectra of the styrene III and bromide IV (Figs. 2 and 3) was used to calculate *cis-trans* ratios and percentage deuteration. (Here and elsewhere, only statistically significant figures are reported for isomeric compositions.) Figure 2 shows the spectra of the following mixtures of III and IIIa.

Fig.	III, %	<i>cis</i> -IIIa, %	<i>trans</i> -IIIa, %
2A	100
2B	18	29	54
2C	36	43	21

Figure 3 is the spectrum of a mixture of the two isomers of the bromide IV containing 82% of the *cis* isomer.

The 1,3-coupling constants in systems such as III and IV have been found to exhibit no simple relationship to the *cis-trans* geometrical configuration.⁹ We find for both III and IV that the *cis* splitting is the larger. The observed splittings are summarized below.

Styrene	Coupling constants, c.p.s.		
	$J_{1,2cis}$	$J_{1,2trans}$	J_{gem}
α -Methyl- (III)	1.5 ± 0.1	0.8 ± 0.1	1.5 ± 0.1
β -Bromo- α -methyl- (IV)	1.50 ± 0.04	1.25 ± 0.04

Structural Assignments for *cis* and *trans*- α -Methyl- β -bromostyrenes (IV).—In order to assign the configuration of the deuterium-labeled diastereomeric dibromides I Ib and I Ic, it was essential to establish the *cis-trans* configurations of the two bromide isomers of IV and thereby those of the α -methylstyrene isomers of IIIa. Both forms of

(9) For a recent review article see R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961).

IV have been previously prepared^{8d,10} by the debrominative decarboxylation of *trans*- α -methylcinnamic acid dibromide. The *trans* (bromine *trans* to phenyl) configuration was assigned to the principal product of the elimination in aqueous solution and the *cis* configuration to the primary product of the reaction performed in dry acetone. These assignments were based on other studies¹¹ of the stereochemistry of debrominative decarboxylation of *trans*-cinnamic acid dibromide in acetone and aqueous solution, in which the principal products were, respectively, *cis*- and *trans*- β -bromostyrene.

We have obtained three further kinds of evidence in support of Flynn's¹⁰ assignment of the *trans* configuration to the higher boiling bromide IV isomer. These are based on physical properties, the mechanism of our synthesis, and selective hydroboration of one isomer in the presence of the other.

In complete correspondence with the physical properties reported^{11a} for the β -bromostyrenes, besides its higher boiling point, *trans*-IV has the higher refractive index, and a higher absorption maximum at longer wave length.

Elimination of hydrogen bromide from the dibromide II with sodium methoxide yields predominantly (94–97%) one isomer of the vinyl bromide IV. Assuming that the dehydrobromination is a *trans* elimination, it is expected that *trans*-IV should be the favored product. That conformation of II which affords *cis*-IV by *trans* elimination is sterically less favorable than that which yields *trans*-IV.

Finally, we have observed that diborane selectively attacks *cis*-IV in dilute diglyme solution. The hydroboration of olefins has been shown¹² in several cases to be sensitive to the steric differences between stereoisomers, the less-hindered *cis* form being the more reactive.

Experimental

Bromination of α -Methylstyrene.—A solution of 126 g. (0.79 mole) of bromine in 80 g. of chloroform was added over a period of 35 min. to 92.3 g. (0.78 mole) of α -methylstyrene (III) dissolved in 100 g. of chloroform contained in a 500-ml. round-bottomed flask which was equipped with a pressure-equalizing dropping funnel and magnetic stirrer and maintained at about -30° by means of a Dry Ice-acetone-bath. The addition was stopped when the bromine color ceased to fade. Most of the solvent was removed at 25° and reduced pressure (finally at 10 mm.). The residual crude dibromide was used directly in the next synthetic step. Distillation of the product at 0.8 mm. pressure or liquid chromatography in hexane on alumina or silicic acid resulted in extensive decomposition.

For the n.m.r. work, 0.4 g. of III was dissolved in 20 g. of chloroform and a 10% solution of bromine in chloroform was added with swirling until the bromine color was not discharged. The solvent was removed at reduced pressure (finally at 10 mm.) with the aid of a rotatory evaporator. The clear, colorless residue was transferred to an n.m.r. tube, diluted slightly with carbon disulfide, degassed and sealed under reduced pressure. Only minor impurities appeared to be present as judged from the n.m.r. spectra.

trans- α -Methyl- β -bromostyrene (*trans*-IV) was prepared by addition of 0.78 mole of crude II from the foregoing pro-

cedure (a strong lachrymator) over a period of 45 min. to a solution of 19.0 g. (0.83 g. atom) of freshly cut sodium in 300 g. of methanol at 0° in a 1-l., round-bottomed, three-necked flask equipped with a mechanical stirrer and a pressure-equalizing dropping funnel. The mixture was stirred while allowed to warm to 25° over 1 hr. and was then poured into a separatory funnel and washed with three 100-ml. portions of water. The crude IV was purified by chromatography (it was difficult to purify by distillation) in 35-g. portions, each dissolved in 10 g. of pentane and run through 2.5-cm. diameter columns containing 160 g. of acid-washed alumina. Only pentane was used for elution, and the collection of 80 ml. of eluate was begun when schlieren first appeared in the receiver. A second fraction of 40 ml. was collected in each case and combined with other such fractions to be re-chromatographed. The total product (since *cis*-IV elutes more slowly than the *trans* isomer, the second fractions are enriched with *cis*-IV and may be kept separate if very pure *trans*-IV is desired) was distilled through a 10-cm. Vigreux column. Three pale yellow fractions were collected, all of which were judged to be free of impurities (except the *cis* isomer) from their n.m.r. spectra. The fractions were analyzed by electronic integration of the n.m.r. peaks of the *cis* and *trans* isomers. The total yield was 81.5 g. (53%).

Fraction	Wt., g.	B.p., $^\circ\text{C}$.	Press., mm.	<i>cis</i> -IV, %	n_D^{25}
1	9.2	55–57.5	0.6–0.7	7	1.5850
2	58.3	58–59	.6–0.7	2	1.5868
3	14.0	58	.6	1	1.5872

Anal. Calcd. for $\text{C}_9\text{H}_9\text{Br}$: C, 54.85; H, 4.60; Br, 40.55. Found: C, 54.88; H, 4.63; Br, 40.90.

A $8.17 \times 10^{-5} M$ solution in cyclohexane of a 8:92 *cis*-*trans* mixture of IV gave at the absorption maximum of 2481 Å. a molar extinction coefficient of 1.60×10^4 liter cm^{-1} mole $^{-1}$. In another preparation, the elimination was carried out at the reflux temperature. The yield was higher (80%) but the reaction mixture contained more of the *cis*-IV (6%).

cis- α -Methyl- β -bromostyrene (*cis*-IV).—A solution of 6.9 g. of 95% *trans*-IV and 1.7 g. of β -acetonaphthone in 100 ml. of hexane was irradiated with a Hanovia type S 200-watt quartz-jacketed light immersed in the liquid for 3.0 hr. and equipped with a filter with a cutoff at 3600 Å. The hexane was then removed on a steam-bath and the crude *cis*-IV was mixed with 2 g. of pentane and chromatographed (see the procedure for preparation of *trans*-IV) on 120 g. of alumina. The first 50 ml. of product-bearing eluate was collected, and after removal of the solvent on a steam-bath afforded 6.2 g. (89%) of IV which was 83% the *cis* isomer. The product of a second isomerization was combined with the first and distilled through a 10-cm. Vigreux column. There was collected 10.2 g. of pale yellow liquid, b.p. 49 – 52° (0.6–0.7 mm.) and n_D^{25} 1.5720. The distillate consisted of 82% *cis*-IV. No isomerization of IV was observed in normal laboratory light or on distillation with the aid of baths at 130° . A $1.61 \times 10^{-4} M$ solution in cyclohexane of a 82:18 *cis*-*trans* mixture of IV gave at the absorption maximum of 2426 Å. a molar extinction coefficient of 1.00×10^4 liter cm^{-1} mole $^{-1}$.

Deuterioacetic acid ($\text{CH}_3\text{CO}_2\text{D}$) was prepared by combining the theoretical amount of D_2O (> 99.5% D) with freshly opened acetic anhydride and swirling the mixture occasionally over a 24-hr. period.

trans- α -Methyl- β -deuteriostyrene (*trans*-IIIa) was prepared from the lithium derivative of *trans*-IV. All glassware was oven-dried overnight. Ethyl ether was distilled from lithium aluminum hydride and stored over Safe-Na. Helium was passed through Fieser solution, sulfuric acid and finally through a glass-wool trap. Bromide IV (19.7 g., 0.10 mole, 98% *trans*) was added all at once at 25° to a stirred suspension of 1.7 g. (0.25 g.-atm.) of lithium wire bits in 75 ml. of ether and contained in a 200-ml., round-bottomed, three-necked flask equipped with a magnetic stirrer, helium inlet and pressure-equalizing dropping funnel. After about 1–2 min., the solution became cloudy and acquired a red-brown color. The flask was then quickly cooled and maintained between -30° and -40° for 40 min., during which time the solution became quite dark. A solution of 7.3 g. (0.12 mole) of deuterioacetic acid in 25 ml. of ether was then added until the color was discharged. The color disappeared after about 50% of the acid had been added. The reaction

(10) E. W. Flynn, Ph.D. Thesis, University of Illinois, 1956, University of Microfilms, Ann Arbor, Mich.

(11) (a) E. Grovenstein and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953); (b) S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2645 (1953);

(12) H. C. Brown and G. Zweifel, *ibid.*, **88**, 1941 (1961).

mixture was poured into a beaker and combined with 100 ml. of pentane. Water was then added dropwise with stirring until the lithium salts had congealed. The liquid was decanted through a filter and dried overnight over anhydrous sodium sulfate. Most of the solvent was removed with the aid of a rotatory evaporator. The n.m.r. spectrum of the residual crude III showed it to be contaminated slightly with the starting material IV and some other impurity, probably methylphenylacetylene.^{3d} The product was diluted with 2 g. of pentane and chromatographed on 150 g. of acid-washed alumina (see the procedure for preparation of *trans*-IV). The first 50 ml. of product-bearing pentane eluate was collected. The solvent was removed on a steam-bath, and, after distillation through a 10-cm. Vigreux column, there was collected 5.0 g. (42%) of material of b.p. 82–85° (61–62 mm.) which consisted of 18% III, 54% *trans*-IIIa and 29% *cis*-IIIa.

cis- α -Methyl- β -deuteriostyrene (*cis*-IIIa) was prepared from 82% *cis*-IV using the same procedure as for *trans*-IIIa except that the vinylolithium intermediate, which is dis-

tinguished by its intense red-brown color, was continuously treated with a 10% ether solution of deuterioacetic acid at a rate just sufficient to keep the solution colorless or slightly yellow throughout the reaction period of 50 min. This reaction was carried out on a 0.018-mole scale, and after chromatography of the product, the yield was 0.85 g. (39%). Analysis by n.m.r. spectrum indicated 36% III, 21% *trans*-IIIa, and 43% *cis*-IIIa with only minor impurities.

Hydroboration of *cis*- and *trans*-IV was carried out in diglyme (methyl ether of ethylene glycol) which had been distilled from sodium. Diborane was generated as required by dropwise addition of 10% solution of boron trifluoride in ether to a 10% solution of sodium borohydride in diglyme. A $5 \times 10^{-3} M$ diglyme solution of a 60:40 *cis*-*trans* mixture of IV was placed in a 0.5 \times 25-cm. thin-walled tube and diborane was bubbled through the solution for intervals of 10–60 sec., depending on the flow rate. After each interval, the *cis*-*trans* ratio was determined by v.p.c. analysis at 185° on acid-washed silicone rubber on Chromosorb. The ratio reached 36:64 after about 60% reaction.

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF A DIMER OF A DERIVATIVE OF CYCLOBUTADIENE

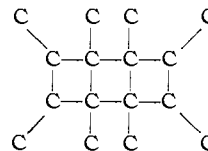
Sir:

In 1960 Kitahara, Caserio, Scardiglia and Roberts¹ described the preparation of a dimer of fluorotriphenylcyclobutadiene ($C_{22}H_{15}F$)₂, (I), which they obtained by the action of phenyllithium on 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene. Although dipole moment measurements, Raman spectra and nuclear magnetic resonance studies have since suggested that the substance might be *anti*-1,2-difluoro-3,4,5,6,7,8-hexaphenyl-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene, other structures have not been ruled out absolutely. We are now completing an X-ray diffraction study of their material and can definitely confirm the stated structure.

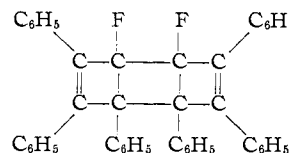
The crystals are colorless triclinic blocks and the primitive unit cell contains two molecules of I (ρ calculated, 1.246 g./cc.; measured, 1.254 g./cc.). There are thus at least $3 \times 46 = 138$ positional parameters to be fixed to establish the positions of the carbon and fluorine atoms alone. This appears to be appreciably larger than any asymmetric unit previously solved without benefit of either heavy atom or isomorphous replacement methods and we did not at first expect to be able to derive a structure, particularly since the molecular skeleton was unknown.

Approximately four thousand nonequivalent X-ray reflections were measured with $CuK\alpha$ rays and statistical studies of these indicated the space-group to be $P\bar{1}$. A three dimensional sharpened Patterson function showed one particularly large, sharp peak which was the right size for the interactions between about sixteen atoms containing a pseudo-center of symmetry and the sixteen atoms related to them by the space-group's center of sym-

metry. With this indication of the location of the "center" of the molecule, a superposition of the Patterson was made with the translation equal to the distance between molecular "centers," and a minimum function was plotted. This eliminates, except for accidental coincidences, all interactions involving atoms not related to another by the pseudo-center in the molecule. The resulting diagram showed approximately the symmetry $2/m$ for a region about the origin and it was possible to account for the peaks with the *trans*-3-ring skeleton shown (with the proviso that two of the



outer C's actually represent fluorine atoms). With this start it was possible by difference maps and low resolution Fourier maps, in three steps, to locate the missing portions of the benzene rings and to show also which atoms are fluorines. Subsequent refinement has reduced the disagreement factor to 16% and the dimensions of the molecule and all intermolecular distances are reasonable, within present standard deviations, which are about $\pm 0.03 \text{ \AA}$. for a bond length. There can thus be no doubt of the correctness of the structure. The bond lengths indicate this basic bond structure



The central C₃ skeleton has very closely the summary $2/m$. The angles between the plane of the cyclobutane ring and the planes of the cyclo-

(1) Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).