D. G. Rea[2] has pointed out that comparative measurements of the anharmonicities of the anomalous C—H vibrations and the normal C—H vibrations would yield information on the intergroup potential function. Alternatively, if a generally applicable potential function is derived from work on barriers to hindered rotation,[3] then the distance-frequency shift relationship can be derived. Distances in rigid molecular structures could then be estimated from infrared data.

Analytically, the observation of this new band suggests the estimation of boat forms of cyclohexane derivatives in mixtures of isomers. Use of the 3050 cm.$^{-1}$ band for the identification of olefinic structures must be made cautiously in cases of complex, rigid structures.

EXPERIMENTAL

Spectrometric measurements. Preliminary survey spectra of compounds I–XI were obtained on a Perkin-Elmer Model 21, double-beam, infrared spectrophotometer with a sodium chloride prism. Quantitative spectra of compounds I–IV were obtained with a different Perkin-Elmer Model 21 infrared spectrophotometer with a lithium fluoride prism. Compounds VIII and α-nopinol were also examined in this spectrophotometer, using a calcium fluoride prism. The spectrum of compound IX in the region 3600–2500 cm.$^{-1}$ was obtained with a Beckman IR-4 spectrophotometer equipped with lithium fluoride prisms by Mr. R. Piccolini at the University of California at Los Angeles. This spectrum was made available to us by Professor S. Winstein. Cells with sodium chloride windows were used. The fused ring compounds were dissolved in carbon disulfide and the spectra of these solutions obtained in the region 3333 cm.$^{-1}$ to 2500 cm.$^{-1}$ in 0.1-mm. cells. A similar cell, filled with solvent, was placed in the reference beam.

The accuracy of the frequency calibration of the Model 21 instrument with lithium fluoride and calcium fluoride prisms was determined by observing the absorption spectrum of a polystyrene film in the C—H stretching region.[4] The frequencies in Table I are accurate to ±2 cm.$^{-1}$ For the cases where the anomalous band was sufficiently resolved, intensities were roughly evaluated using Ramsay's Method I[5] and are probably no more accurate than ±20%. This accuracy is sufficient for our purposes.

Source of compounds. α-Nopinol (m.p. 101.5–102.5°) was prepared from a sample of the acid phthalate (m.p. 128–130°) for which we are indebted to Professor S. Winstein. The structure of α-nopinol has been investigated by Winstein and Holness,[6] who conclude it is an equilibrium mixture of two isomers. The isomer with the structure shown in Fig. 1 predominates (75%).

The preparation of compound I has been described by S. B. Soloway,[7] and a sample was kindly made available to us by Julius Heiman and Company, Denver, Colo. Compounds II–VII have been briefly described by S. Winstein.[8] The details of structure assignment and preparation have been presented in a recent publication.[9] Compounds VIII and IX are derived from the diketone, X.[8,10] This diketone was converted into a monoketone, XI, by Wolff-Kishner reduction of its monoketal, followed by hydrolysis of the reduced monoketal. Lithium aluminum hydride reduction of this monoketone yields the alcohol, VIII. Dehydration of VIII followed by hydrogenation[11] yielded the hydrocarbon, IX. Details of the preparation and structure assignments of compounds VIII and IX will be presented in forthcoming publications.

Acknowledgment. We are indebted to Professor S. Winstein for suggesting that α-nopinol and the hydrocarbon IX should show the anomalous bands and for providing us with a sample of α-nopinol acid phthalate and the spectrum of IX.

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Long Range Splittings in the NMR Spectra of Isomeric 2-Bromo-2-butenes[1,2]

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The recent publication of Fraser[4] on long-range coupling between the protons in the methyl groups of tiglic and angelic acids and their methyl esters prompts us to report a similar observation in the NMR spectra of *cis*- and *trans*-2-bromo-2-butene. In this case, also, we observe coupling between the methyl group protons that are separated from one another by five bonds (four single bonds and one double bond). Furthermore, the magnitude of this coupling is larger when the two methyl groups are *trans* disposed about the olefinic linkage than when they are *cis* oriented. The possibilities of such splittings have been alluded to previously to account for the barely perceptible fine structure in one of the peaks in the NMR spectrum of methyl photosantonate.[5] Such splittings across five bonds have also been observed in the NMR spectra of

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(3) This investigation was carried out during the tenure of a Predoctoral Fellowship from the National Institute of Allergy and Infectious Diseases, U. S. Public Health Service.

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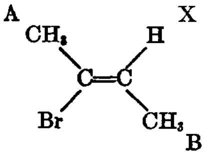
TABLE I

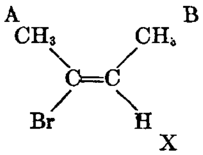
	A	B	X	J_{AX}	J_{BX}	J_{AB}
cis-2-Bromo-2-butene	266	300	46	1.42 ± 0.05	7.06 ± 0.06	1.12 ± 0.04
trans-2-Bromo-2-butene	262	296	48	1.36 ± 0.06	6.39 ± 0.04	1.59 ± 0.03

plumericin[6] and in the spectra of other butene derivatives.[7]

The NMR spectra of pure *cis*- and *trans*-2-bromo-2-butene[8] were observed at 60 Mc with a Varian Associates high resolution spectrometer (Model 5-4300 V) equipped with a superstabilizer. Calibration was accomplished by the audio sideband technique. The chemical shifts are reported relative to benzene as an external standard.



trans-2-bromo-2-butene



cis-2-bromo-2-butene

In both isomers, the protons of the B-methyl group were observed as a doublet of quartets. The centers of each quartet were separated by 7.06 ± 0.06 c.p.s. (*cis* isomer) and 6.39 ± 0.04 c.p.s. (*trans* isomer). The separation between the lines of the quartets was 1.12 ± 0.04 c.p.s. (*cis* isomer) and 1.59 ± 0.03 c.p.s. (*trans* isomer). The protons of the A-methyl group gave an absorption that consisted of a quintet of lines with relative areas 1:4:6:4:1 with the distance between the lines being about 1.2 c.p.s. (for the *cis* isomer) and about 1.5 c.p.s. (for the *trans* isomer). The alternate assignment of the NMR absorptions for the two methyl groups is eliminated on the basis of two arguments. Firstly, the proton in the methyl group nearer the bromine would be expected to be seen at a less shielded, lower field position in agreement with our assignment. Secondly, the alternate assignment would result in unreasonable coupling constants[9]; *e.g.*, for *cis*-2-bromo-2-butene the reverse assignment leads to $J_{BX} = 1.4$ c.p.s., $J_{AX} = 7.0$ c.p.s. The absorption of the X proton consisted of a quartet of quartets. The distance between the quartets was 7.06 c.p.s. (*cis* isomer) and 6.39 c.p.s. (*trans* isomer). The separation of the lines within each quartet was 1.42 ± 0.05 c.p.s. (*cis* isomer) and 1.36 ± 0.06 c.p.s. (*trans* isomer). These observations lead directly to the coupling constants reported in Table I.

In agreement with Fraser[4] we find that the *cis* and *trans* five-bond interactions, although diminished in magnitude, bear the same relationship to one another as the coupling constants for *cis* and *trans* vinyl protons,[10] which fact renders this a potentially useful technique for the determination of the geometry about an appropriately substituted olefin. We also observe that the four-bond interactions are apparently greater when the groups are in the *trans* than in the *cis* configuration, though this difference is only one standard deviation.

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