IBM 704 computer, making use of the FREQINT IV program kindly supplied by Dr. A. A. Bothner-By of Mellon Institute. N-Deuterated DNP's were prepared by treating the DNP solution (in CH₂Br₂) with D₂O directly in n.m.r. sample tubes.

The two-phase systems were shaken vigorously by hand for a few minutes at convenient intervals. The progress of the ex-change could thus be readily followed by merely allowing the two phases to separate, the lower, organic phase being made

long enough to keep the D₂O well above the critical region of the sample tube. Such equilibrations, run at room temperature without added catalysis, were usually complete in one or two davs.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

The Nuclear Magnetic Resonance Spectra of Cyclopropane Derivatives¹

BY KENNETH B. WIBERG² AND BERNARD J. NIST

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The n.m.r. spectra of cyclopropanecarboxylic acid, cyclopropyl bromide, and of 1-methyl and 1-phenylcyclo-propane-*cis*-1,2-dicarboxylic acids have been analyzed. The spectral parameters are discussed in relationship to values found in other compounds.

The n.m.r. spectra of rigid molecules are of interest for two reasons. First, they permit an experimental correlation of chemical shifts and coupling constants with geometry, and this is of importance in testing theories dealing with these quantities. Second, the structural details of these compounds may often be determined for an analysis of the spectrum, particularly if the spectra of some model compounds are available. In order to obtain more data which may be useful in these connections, we have begun an investigation of some simple cyclopropane and cyclobutane derivatives. The results for some of the cyclopropane compounds are given here.

$$\nu_{\rm A} = 546.2 \text{ c.p.s.}$$
 $\nu_{\rm B} = 540.4 \text{ c.p.s.}$
 $J_{\rm AA'} \sim J_{\rm BB'}(cis) = 11.0 \text{ c.p.s.}$ $J_{\rm AB}(gem) = -4.1 \text{ c.p.s.}$
 $J_{\rm AB'}(trans) = 7.0 \text{ c.p.s.}$

It can be seen that the *cis* coupling constant is larger than the *trans* constant, as expected based on the dihedral angles involved.⁵

Approximate values for the coupling with the 2proton of cyclopropanecarboxylic acid were easily obtained from the resonance bands corresponding to this proton. Using the above parameters and those for the 2-proton, it was possible to obtain the "best" parameters using an iterative program for an IBM-709

TABLE I						
N.M.R. SPECTRA	OF CYCLOPROPANE	DERIVATIVES				

			Chemical	C	oupling constants, c.p.s	
Compound		Proton	shift, τ	cis	trans	gem
H_{5} H_{2} H_{2} H_{2} H_{1}	R = COOH	$ \begin{cases} 1 \\ 2(4) \\ 3(5) \end{cases} \\$	$8.42 \\ 9.03 \\ 8.94$	$\begin{array}{c} 8.0(1,2)\\ 10.5(2,4)\\ 11.0(3,5) \end{array}$	$\begin{array}{c} 4.6(1, 3) \\ 7.5(2, 5) \end{array}$	-4.3
	R = Br	$ \begin{cases} 1 \\ 2(4) \\ 3(5) \end{cases} \\$	7.169.009.12	$7.3(1, 2) \\10.3(2, 4) \\10.0(3, 5)$	3.9(1, 3) 6.6(2.5)	-5.9
HO_2C R HO_2C HO	$R = C_6 H_5$	$\begin{cases} 1\\ 2\\ 3 \end{cases}$	$7.63 \\ 8.44 \\ 7.92$	8.6(1,2)	6.2(1,3)	-5.2
R	$R = CH_3$	${1 \\ 2 \\ 3}$	8.02 8.77 8.32	8.2(1, 2)	6.3(1,3)	-5.0

Monosubstituted cyclopropanes are of particular interest since they permit a determination of all of the coupling constants for the systems. However, the analysis of the resultant A2B2C spectrum is not readily accomplished without a knowledge of the approximate values of chemical shifts and coupling constants. The spectrum of cyclopropanecarboxylic acid may be simplified by preparing the α -deuterio derivative which will then give an A_2B_2 spectrum (Fig. 1). From the relative intensities, it was apparent that one of the coupling constants had a sign opposite to that of the others³; the spectral parameters were then easily found, giving at 60 Mc.⁴

(1) This work was supported by an A. P. Sloan Foundation fellowship to K. B. W.

(2) Department of Chemistry, Yale University, New Haven, Conn.

(3) This was easily seen by a comparison of the observed spectrum with those given in K. B. Wiberg and B. J. Nist, "Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) The chemical shifts are given with respect to tetramethylsilane (600.0). The difference in shape of the two halves of the spectrum is presumably due to the difference between the cis and trans coupling constants between hydrogen and deuterium. We wish to thank Dr. R. Eisenthal for preparing the sample of cyclopropane- α -d₁-carboxylic acid used in this work.

computer.⁶ The values obtained for the 60-Mc. spectrum are given in Table I, and gave the spectrum shown in Fig. 2.7 It was not possible to fit the spectrum if the gem coupling constant was taken as positive. In analogy with the relative magnitudes of the coupling constants for the A_2B_2 part, the larger of the constants, $J_{\rm AC}$ and $J_{\rm BC}$ was assigned as the *cis* constant and the smaller as the trans constant. Thus, the carboxyl group gives a larger chemical shift for the *cis*-hydrogens than for the trans-hydrogens.

Whereas the values of the vicinal coupling constants are in good agreement with those expected from the theoretical treatments of spin-spin coupling,^{5,8} the values of the gem constants do not agree. The latter

(7) The spectrum was also obtained at 40 Mc., and an excellent fit was obtained using these parameters.

(8) M. Karplus, J. Chem. Phys., 30, 11 (1959); M. Karplus and D. H. Anderson, ibid., 30, 6 (1959)

⁽⁵⁾ Cf. H. Conroy in "Advances in Organic Chemistry, Methods and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 308-311.

⁽⁶⁾ We wish to thank Drs. J. D. Swalen and C. A. Reilly for supplying us with this program. Cf. J. D. Swalen and C. A. Reilly, J. Chem. Phys., 37, 21 (1962).

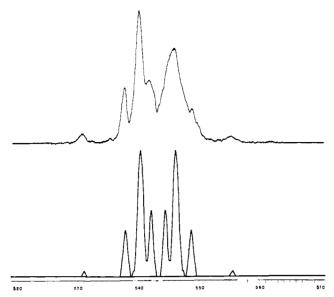


Fig. 1.—The upper spectrum is that observed for cyclopropane-1-*d*-carboxylic acid, and the lower is the spectrum which has been calculated and plotted by an IBM-709 computer. The reference (600 sec.⁻¹) was tetramethylsilane and the radiofrequency was 60 Mc.

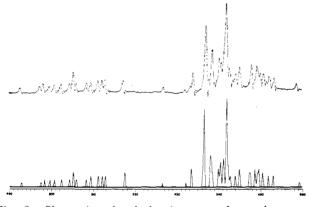


Fig. 2.—Observed and calculated spectra for cyclopropanecarboxylic acid.

are predicted to have the same sign as for the vicinal constants,^{8,9} but for most compounds the signs are found to be opposite.¹⁰ Among saturated compounds, the only exceptions are styrene oxide, other mono-substituted ethylene oxides, and β -p-nitrophenyl- β -propiolactone.^{9,11} One might be tempted to suggest that some electronic factor involved in forming a small ring were responsible for the difference between the two groups of cases, but this is evidently incorrect since the *gem* constant for the cyclopropane ring is also of opposite sign to the vicinal constants.

The spectrum of bromocyclopropane¹² is quite different from that for the acid (Fig. 3). By using some estimated coupling constants and the iterative program

(9) H. S. Gutowsky, M. Karplus, and D. M. Grant, J. Chem Phys., **31**, 1278 (1959).

(10) R. R. Fraser, R. U. Lemieux, and J. D. Stevens, J. Am. Chem. Soc.,
83, 3901 (1961); C. A. Reilly and J. D. Swalen, J. Chem. Phys., 35, 1522 (1961); F. Kaplan and J. D. Roberts, J. Am. Chem. Soc., 83, 4666 (1961); R. R. Fraser, Can. J. Chem., 40, 1483 (1962); H. S. Gutowsky and C. Juan, J. Chem. Phys., 37, 120 (1962); K. A. McLauchlan and D. H. Whiffen, Proc. Chem. Soc., 144 (1962); H. Finegold, *ibid.*, 213 (1962); R. Freeman, K. A. McLauchlan, J. 1. Musher, and K. G. R. Pachler, Mol. Phys., 5, 321 (1962).

(11) C. A. Reilly and J. D. Swalen, J. Chem. Phys., 32, 1378 (1960);
 35, 1522 (1961); D. D. Elleman and S. L. Manatt, J. Mol. Spectry., 9, 477 (1962).

(12) We wish to thank Dr. J. D. Roberts for supplying a sample of this compound.

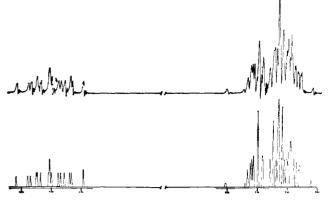


Fig. 3.—Observed and calculated spectra for cyclopropyl bromide.

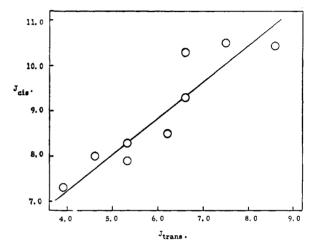


Fig. 4.—Correlation of *cis* and *trans* coupling constants for hydrogens on a given carbon in cyclopropane derivatives.

mentioned above, it was possible to obtain the parameters for the 60-Mc. spectrum, and these are given in Table I. The calculated spectrum based on these parameters is given in Fig. 3. The spectrum was also obtained at 40 Mc. and a comparison with the calculated spectrum showed an excellent fit.

If we again make the assumption that the *cis* coupling constant is larger than the *trans* constant, we are led to the conclusion that the bromine gives a larger chemical shift for the methylene protons *trans* to it than for the *cis*-protons. Regardless of how one may choose to assign the parameters, the effect of the bromine is opposite to that of the carboxyl group.

Two simpler ABC systems, I-methylcyclopropanecis-1,2-dicarboxylic acid and 1-phenylcyclopropanecis-1,2-dicarboxylic acid, were also studied and gave the parameters indicated in Table I.¹³ Here also, the spectrum could be fit only by assuming that the gem coupling constant had a sign opposite to that of the other vicinal constants.

A number of other cyclopropane ABC spectra have previously been reported by Graham and Rogers¹⁴ and by Smidt and deBoer.¹⁴ If one examines all of the available data, one finds there is a rough relationship between the *cis* and *trans* coupling constants for a given group of protons. This is examined in more detail in Fig. 4. It can be seen that the correlation is general, but with large deviations. Such a correlation might be anticipated based on the work of Glick and Bothner-By.¹⁵ The *gem* constants were found to be

(13) Samples of these compounds were kindly supplied by Dr. L. L. McCoy.

- (14) J. D. Graham and M. T. Rogers, J. Am. Chem. Soc., 84, 2249 (1962);
 J. Smidt and Th. J. deBoer, Rec. trav. chim., 79, 1235 (1960).
- (15) R. E. Glick and A. A. Bothner-By, J. Chem. Phys., 25, 362 (1956).

negative in the compounds reported herein, and probably are negative in the previously reported cyclopropanes. The values of the *gem* constant vary over a considerable range (-4.3 to -8.4 c.p.s.). The larger values are associated with the 1,1-dichloro derivatives; the other compounds have values of -5 ± 1 c.p.s.

In the case of cyclopropanecarboxylic acid, 1-methylcyclopropane-1,2-dicarboxylic acid, 1-phenylcyclopropane-1,2-dicarboxylic acid, and cyclopropane-1,1,2tricarboxylic acid, the chemical shift for the protons *cis* to an electron-withdrawing group is larger than that for the protons *trans* to this group. With bromocyclopropane and the other compounds previously reported, the relationship is reversed. There are not enough data available to permit making generalizations; however, the latter behavior appears characteristic of the groups -Br, -OR, and $-C_6H_5$. It will be necessary to examine more monosubstituted compounds and this is planned.

Experimental

N.m.r. Spectra.—The spectra were determined using a Varian DP-60 n.m.r. spectrometer using both 40 and 60 Mc. Cyclopropanecarboxylic acid was examined as a 10% solution in carbon tetrachloride, cyclopropyl bromide was run neat, and the dicarboxylic acids were run as 15% solutions in deuterium oxide. Tetramethylsilane was used as the reference for the first two compounds, and 2,2-dimethyl-2-silylpentane-5-sulfonate was used as the reference in deuterium oxide.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, AGRICULTURAL CHEMICALS DIVISION, MONSANTO CHEMICAL CO., St. Louis 66, Mo.]

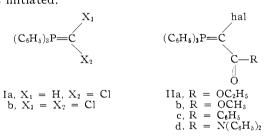
Reactions of Phosphorus Compounds. VII. Carbanion Stabilization and Resulting Effects on P-Ylid Reactivity

BY A. J. SPEZIALE AND K. W. RATTS

RECEIVED APRIL 3, 1963

The reactivity of a series of resonance-stabilized halo-ylids has been investigated and related to infrared spectral data and to basicity. Steric effects, carbanion delocalization, and stereochemistry have been correlated with reactivity; certain generalizations have been made concerning the mechanism of the Wittig reaction with halo-ylids.

Halo-ylids I and II have recently been synthesized and shown to be valuable intermediates in the preparation of haloolefins.¹⁻⁶ The isolation of resonancestabilized halo-ylids⁴⁻⁶ provides a series of compounds which allows a direct study of the influence of adjacent halogen atoms and phosphorus d-orbitals upon carbanion stabilization. For these reasons an investigation of the reactivity of resonance-stabilized haloylids and the stereochemistry of the Wittig reaction was initiated.



Vlids of type II are less reactive than type I owing to charge delocalization (III-V) which decreases nucleophilicity.

A marked shift in the C==O stretching frequency from the normal C==O region must be due to contributions such as IV to the resonance hybrid. Since both reactivity and ν_{CO} are related to charge delocalization, it was of interest to determine if reactivity could be predicted from infrared data. The C==O stretching frequencies for a series of these ylids are listed in Table I. In the ester ylids R==OC₂H₅ or OCH₃,

A. J. Speziale and K. W. Ratts, J. Am. Chem. Soc., 84, 854 (1962).
 (a) D. Seyferth, S. Grim, and T. O. Read, *ibid.*, 82, 1510 (1960);

- (b) G. Wittig and M. Schlosser, Angew. Chem., 72, 324 (1960).
 (3) R. Rabinowitz and R. Marcus, J. Am. Chem. Soc., 84, 1312 (1962).
 - (3) R. Rabinowitz and R. Marcus, J. Am. C.
 (4) G. Markl, Chem. Ber., 94, 2996 (1961).
 - (4) G. Marki, *Chem. Dett.*, **92**, 2000 (1961).
 (5) D. B. Denney and S. T. Ross, *J. Org. Chem.*, **27**, 998 (1962).
 - (6) A. J. Speziale and K. W. Ratts, *ibid.*, **28.** 465 (1963).

changes in X from hydrogen to halogen result in a shift of the C=O absorption to higher frequency. The additional delocalization of the carbanionic charge in III by halogen (VI) decreases the contribution of IV to the resonance hybrid.

$$\begin{array}{c} & & \\ & & \\ \mathbf{R}_{\vartheta}^{\oplus} \mathbf{P} - \mathbf{C} - \mathbf{C} \\ & \parallel \\ \mathbf{VI} & \mathbf{X} \ominus \end{array}$$

The C–O bond is shortened and the shift in frequency is, therefore, in the expected direction.

TABLE I				
Infrared Spectra (Stretching Frequency of $C=0$) of				
YLIDS AND PHOSPHONIUM SALTS (CHCl ₃)				

	X O		
(C6H5)3P=	=CCR		ν _{CO} phosphon.
x	R	$\nu_{\rm CO}$ ylid (cm1)	ium salt (cm1)
Н	OC_2H_5	1610	1725^{a}
Cl	OC_2H_5	1625	
Br	OC_2H_5	1625	
H^b	OCH_3	1621	
$C1^b$	OCH_3	1642	
Br^b	OCH_3	1658	
I ^b	OCH_3	1642	
Н	C_6H_5	1500	1670^{c}
C1	C_6H_5	1470	1675°
Br	C_6H_5	1465	1660^{a}
I	C_6H_5	1465	
Н	$N(C_6H_5)_2$	1530	1650°
C1	$N(C_6H_5)_2$	1510	
Br	$N(C_6H_5)_2$	1490	
CH_3^{d}	OCH_3	1584	
$CO_2C_2H_5^*$	$OC_2H_{\mathfrak{d}}$	1695, 1655,	
		1615	

^a Bromide salt. ^b Determined in KBr; see ref. 4. ^c Chloride salt. ^d Ref. 8. ^e L. Horner and H. Oediger, *Chem. Ber.*, 91, 437 (1958).