(boiling range 108–115° (2 mm.)). The mixture of C_8-benzoates was hydrogenated over platinum at atmospheric pressure and room temperature quantitatively to 1-benzoxy-2-ethylhexane. The two isomeric octenyl benzoates were formulated as: 1-benzoxy-2-ethylhexene-3 and -4. In addition there was formed a material which analyzed for dibenzoxyhexadecene (boiling range 200–215° (1 mm.). *Anal.* Calcd. for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68; ester value, 0.431; mol. wt., 464; bromine no., 34. Found: C, 77.3, 77.5; H, 8.2, 8.1; ester value, 0.424, 0.428, mole. wt., 420; bromine no., 31, 27, 38.

In addition to ester products a mixture of butyl- and butenylbenzene isomers were fromed in 5–10% yields. They were not characterized. Benzene was not determined quantitatively.

The presence of 2-benzoxybutene-2 (−1) could not be detected in the reactions of butene-2. The crude reaction mixture was directly treated with Claisen alkali, neutralized and distilled. The distillate on treatment with DNP reagent yielded no methyl ethyl ketone-DNP. The mixture from butene-1 gave on similar treatment a small amount of propionaldehyde-DNP (m.p. 152–153°). In a similar manner, the crude reaction mixture from butene-2 and benzoyl peroxide with copper salts was distilled directly into an ice trap at atmospheric pressure to remove solvent and any material boiling less than 100°. The distillate was examined by G.L.C. (10-foot Ucon polar on Chromosorb W at 65°) but showed no methyl ethyl ketone (14.5′, benzene, 18.5′). Direct examinations of the crude reaction mixture and the distilled ester reactions also gave no indication of the presence of 2-benzoxybutene-1 or −2 (*vide supra*).

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[CONTRIBUTION FROM THE PHYSICAL SCIENCES DIVISION, JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

A Double Resonance Study of the N.m.r. Spectrum of 1-Chlorobutadiene-1,2 and the Determination of the Relative Signs of the Coupling Constants

BY STANLEY L. MANATT AND DANIEL D. ELLEMAN

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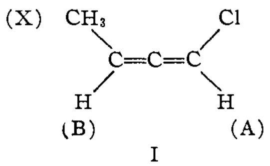
The 60 Mc. proton n.m.r. spectrum of 1-chlorobutadiene-1,2 has been studied by the audio side-band phase detection proton–proton decoupling method. Selective irradiation of certain of the spectral lines of one set of equivalent nuclei with a $\gamma H_1/2\pi$ of the order of the J's was carried out while simultaneously recording the transitions of the other nuclei. From interpretation of the changes in the decoupled regions of the spectrum, the relative signs of J_{AB} and J_{BX} were determined to be different. Reasons why it is not possible to determine the relative signs between J_{AB} and J_{AX} by this double resonance technique are discussed. An assignment of the absolute signs with J_{BX} and J_{AX} being positive and with J_{AB} being negative has been made on the basis of the present work, the theoretical work of Karplus and the high-resolution work of Snyder and Roberts.

Introduction

From a complete analysis of the proton high-resolution n.m.r. spectra of 1-chlorobutadiene-1,2 (I) at 40 and 60 Mc., it was not possible to determine the sign of J_{AB} relative to the signs of J_{AX} and J_{BX}.[1] The present work was undertaken to see if Freeman's[2] double resonance technique for the determination of the relative signs of proton–proton coupling constants could be applied to the 1-chlorobutadiene-1,2 (I) molecule. The results of such experiments were expected to be of general interest in light of Karplus' recent theoretical work on the π-electron contribution to proton–proton coupling constants.[3]



I

The first steps in applying Freeman's method for sign determination are to try to label each transition of the spectrum according to its origin in the limit as all the ratios J_{ij}/δ_{ij} approach zero (J_{ij}, coupling constant between nuclei i and j, δ_{ij}, chemical shift between nuclei i and j) and then to write down for each transition the spin states of all the neighboring nuclei which are coupled to the nucleus responsible for that particular transition. For an ABX_3 system there is usually no question as to the assignments in the X_3 region. An approximate assignment of the origin of the lines can usually be made in the AB region even if there is some overlap of the lines of these protons. To assign the spin states of the neighboring nuclei one proceeds as follows: the first-order expression for the resonance line positions of a set of equivalent nuclei i is $\delta_i + \Sigma J_{ij} m_j$ where m_j is one of the possible values of the magnetic quantum number for a set of equivalent nuclei j coupled with i. The components which make up a particular m_j are the appropriate neighboring nuclear spin states. The X_3 neighboring nuclear spin states of the A proton transitions are obtained from the four possible values of m_{X_3}, $+^3/_2$, $+^1/_2$, $-^1/_2$ and $-^3/_2$ corresponding to spin states $\alpha\alpha\alpha$, $\alpha\alpha\beta$, $\alpha\beta\beta$ and $\beta\beta\beta$, respectively. The B neighboring nuclear spin states of the A proton transitions are obtained from the two possible values of m_B, $+^1/_2$ and $-^1/_2$ corresponding to spin states α and β, respectively. Thus, for each of the observed A transitions, m_B and m_{X_3} values can be assigned for a particular choice of the signs of J_{AB} and J_{AX}. Similar arguments can be used to obtain the neighboring nuclear spin states of the B and X_3 transitions.

Figures 1a and 2a show the X_3 and AB regions, respectively, of the n.m.r. spectrum of I recorded at 60 Mc. with each transition numbered. For I it is quite easy to make a complete assignment because the A and B regions do not have any overlapping lines. Thus lines 1–8 belong to nucleus

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[1] E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962).

[2] R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321 (1961); private communication from R. Freeman.

[3] M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

TABLE I

SPIN STATES OF NEIGHBORING NUCLEI FOR COUPLING CONSTANTS ALL THE SAME RELATIVE SIGN[a]

Origin Transitions	A								B								X_3			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A									α	β	α	β	α	β	α	β	α	β	α	β
B	α	α	α	β	α	β	β	β									α	α	β	β
X_3	$\alpha\alpha\alpha$	$\alpha\alpha\beta$[b]	$\alpha\beta\beta$	$\alpha\alpha\alpha$	$\beta\beta\beta$	$\alpha\alpha\beta$	$\alpha\beta\beta$	$\beta\beta\beta$	$\alpha\alpha\alpha$	$\alpha\alpha\alpha$	$\alpha\alpha\beta$	$\alpha\alpha\beta$	$\alpha\beta\beta$	$\alpha\beta\beta$	$\beta\beta\beta$	$\beta\beta\beta$				

[a] If J_{AB} and J_{BX} have different signs, row B of column A or row B of column X should have the α's and β's interchanged. Only one of the possible permutations of the X_3 spin states for m_{X_3} equal $^1/_2$ and $-^1/_2$ is given.

A and lines 9–16 to nucleus B. Table I gives the spin states for the neighboring nuclei for each transition and was constructed as described above with the assumption that all the coupling constants (*i.e.*, J_{AB}, J_{AX} and J_{BX}) have the same relative sign. For the case of J_{AB} different from J_{AX} and J_{BX} in relative sign, the α's and β's should be interchanged in row B of column A and row A of column B of Table I. If J_{BX} has a different sign from J_{AB} and J_{BX} then row X of column B and row B of column X in Table I should have the α's and β's interchanged. For J_{AX} different from J_{AB} and J_{BX}, row X of column A and row A of column X should be interchanged. It should be noted that if all the α's and β's are interchanged in Table I or any of the variations described above, no changes in the conclusions reached below will result.

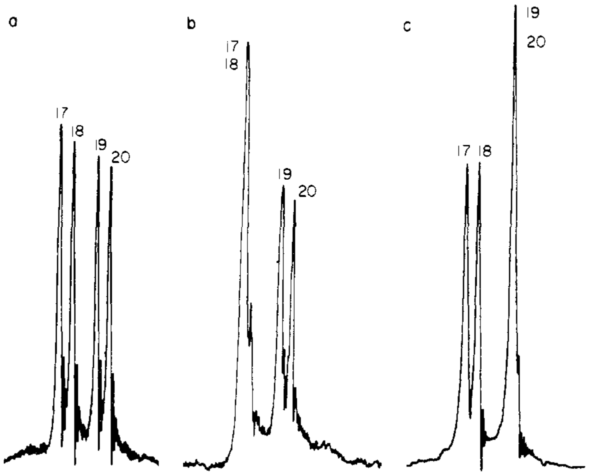

Fig. 1.—Methyl protons of 1-chlorobutadiene-1,2: a, undecoupled phase detected; b, decoupled phase detected with Ω = 245.0 c.p.s., $\gamma H_1/2\pi$ = 8.9 c.p.s.; c, decoupled phase detected with Ω = 258.0 c.p.s., $\gamma H_1/2\pi$ = 8.9 c.p.s. In all cases increasing field is to the right.

The condition for destroying the coupling between two sets of nuclei i and j, by double irradiation is that at one of the resonance positions a $\gamma H_1/2\pi$ of the order of or greater than J_{ij} (all in c.p.s.) be applied while the other set is observed in resonance.[4] We have been able to irradiate selectively certain transitions of a particular set of equivalent nuclei in I while simultaneously observing the effect on the transitions of the other two sets of nuclei.

Experimental

The 1-chlorobutadiene-1,2 was the sample used by Snyder and Roberts.[1] Spectra were obtained with a Varian model V-4311 60 Mc. spectrometer with 12-inch Varian magnet equipped with a VK-3506 Super Stabilizer.

The proton spin decoupler employed in the present experiments utilizes the audio side-band phase detection techniques described by Kaiser[5] and Freeman[6] and is described elsewhere.[7] The H_1 field was calibrated as described by Anderson.[8] All frequencies were measured with a Hewlett-Packard model 524-C frequency counter.

Results

From Fig. 2a it can be seen that the A region of I can be decomposed into two overlapping quartets as can the B region. The X_3 region is a simple quartet. The complete spectrum has been analyzed by Snyder and Roberts.[1] Double irradiation experiments were performed at a number of frequencies between 200 and 258 c.p.s. and at a number of H_1 levels. Figures 1b and 1c show the changes produced in the X_3 region by irradiation at 245 and 258 c.p.s., respectively, with $\gamma H_1/2\pi$ = 8.9 c.p.s. A frequency of 258 c.p.s. corresponds to selective irradiation close to lines 1, 2, 3 and 5 of the A region. This caused the collapse of lines 17 and 18. At a frequency of 245 c.p.s. lines 4, 6, 7 and 8 were being irradiated, and lines 19 and 20 collapsed. At a frequency of 251 c.p.s. (which is about the chemical shift between A and X_3) we observed that the doublets 17, 18, and 19, 20 were equally collapsed. The AB region was observed at the same three frequencies as shown in Figs. 2b, 2c and 2d. It is interesting to note that at the frequencies of 245 and 258 c.p.s. in each case one of the quartets of the A region has completely collapsed to a singlet while the remainder of the spectrum is only slightly perturbed. At a frequency of 251 c.p.s. the two overlapping quartets of the A region have collapsed to the extent that they no longer overlap as shown in Fig 2d. All these irradiation experiments were carried out at a $\gamma H_1/2\pi$ of about 8.9 c.p.s. It was possible to decouple completely the methyl group from the AB protons as shown in Fig. 2f with a $\gamma H_1/2\pi$ of 112 c.p.s. We were also able to decouple selectively the A proton completely from the X_3 proton with a $\gamma H_1/2\pi$ of 45 c.p.s.; the B region lines were strongly perturbed in this case. In a similar manner the B region could be collapsed to a doublet (not shown). To accomplish this required a $\gamma H_1/2\pi$ of the order of 100 c.p.s.

We observed that in order to obtain reproducible decoupled spectra at large H_1's it is necessary to sweep through a decoupled region and then wait

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(4) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955).

(5) R. Kaiser, *Rev. Sci. Instr.*, **31**, 963 (1960).

(6) R. Freeman, *Mol. Phys.*, **3**, 435 (1960).

(7) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, in press (1962).

(8) W. A. Anderson, "NMR and EPR Spectroscopy," by Varian Staff and Consultants, Pergamon Press, New York, N. Y., 1960, pp. 180–184.

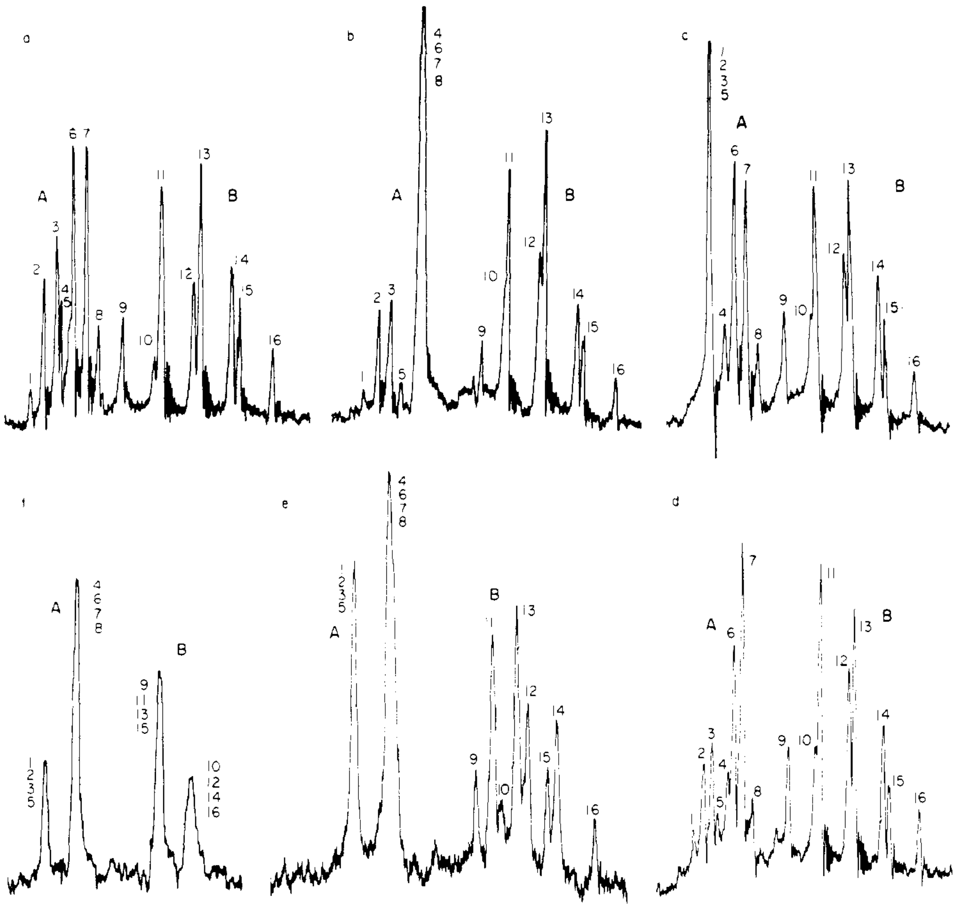

Fig. 2.—Allenic proton region: a, undecoupled phase detected; b, decoupled phase detected with $\Omega = 245.0$ c.p.s., $\gamma H_1/2\pi = 8.9$ c.p.s.; c, decoupled phase detected with $\Omega = 258.0$ c.p.s., $\gamma H_1/2\pi = 8.9$ c.p.s.; d, decoupled phase detected with $\Omega = 251.5$ c.p.s., $\gamma H_1/2\pi = 8.9$ c.p.s.; e, A proton completely decoupled from X_3 protons, $\Omega = 250.5$, $\gamma H_1/2\pi = 45$ c.p.s.; f, AB region completely decoupled from X_3 protons, $\gamma H_1/2\pi = 112$ c.p.s. In all cases increasing field is to the right.

as long as a minute or so before resweeping the same region. At high H_1 we found that the relative line positions and degree of decoupling are markedly sweep dependent as would be expected.

Interpretation of Results

The results of the selective double irradiation experiments described above have been interpreted by consideration of the spin states of the neighboring nuclei for each transition as shown in Table I. Irradiation of the lines 1, 2, 3 and 5 does *not* strongly perturb transitions 4, 6, 7 and 8 as discussed above. The former transitions all have nucleus B in the α state if all the coupling constants have the same sign. Physically, when lines 1, 2, 3 and 5 of A are irradiated while observing X_3, the A and X_3 protons should be decoupled only in those molecules which have proton B in spin state α. Thus if the X_3 spectrum is simultaneously observed we would expect that lines 17 and 18 would collapse. Likewise when lines 4, 6, 7 and 8 are irradiated while observing the X_3 region, A and X_3 should be decoupled only in those molecules with proton B in spin state β. Thus lines 19 and 20 should collapse. Experimentally what is observed (see Fig. 1) is just the opposite to that described above. Irradiation of lines 1, 2, 3 and 5 collapses lines 17 and 18, and irradiation of lines 4, 6, 7 and 8 collapses lines 19 and 20. If J_{AB} and J_{BX} have different signs all the α's and β's should be interchanged in row B of column A or alternately in row B of column X of Table I. From this new table one predicts just what is observed experimentally, *i.e.*, lines 1, 2, 3 and 5 collapse when lines 19 and 20 are irradiated and lines 4, 6, 7 and 8 collapse when lines 17 and 18 are irradiated; thus J_{AB} has a different sign from J_{BX}.

The question remained in our minds as to whether it would be possible to irradiate certain lines in the B region while observing the X_3 region and to interpret the resulting changes of the spectral lines in terms of the relative signs of J_{AB} and J_{AX}. From Fig. 2a it can be seen that the two quartets of the B region overlap significantly. Lines 9 through 16 alternate with the A nucleus having spin states α, β, α, β, α, β, α, β, respectively. Because of this alternation of the spin states of the A nucleus and the overlap of the two quartet multiplets of the B region, the resulting changes of the decoupled spectra were predicted to be quite complex and not easily interpretable. It should not be possible to irradiate selectively a majority of the lines with either the α or β spins without irradiating a majority of the other. Our experiments verified this prediction. No information as to the relative sign between J_{AB} and J_{AX} could be obtained from the complex patterns observed.

In principle it should be possible to obtain the relative sign between J_{AX} and J_{BX} by irradiation between A and B, but this is not feasible experimentally because the chemical shift difference is only of the order of 25 c.p.s.; thus the two decoupled AB regions will overlap in the audio sideband phase detection technique.[5]

Discussion

Although for some time it was considered that proton–proton coupling constants were all of the same sign, *i.e.*, positive, this notion was overthrown first experimentally by Alexander[9] and since by other workers[10] and theoretically by the work of Karplus[3] on the π-electron contribution to the spin coupling constants.

In the present work it was determined that J_{AB} has a different relative sign from J_{BX} in 1-chlorobutadiene-1,2, but the problem of the absolute signs cannot be settled experimentally by the method used. Snyder and Roberts[1] have been able to determine that J_{AX} and J_{BX} have the same signs from high resolution analysis, but they could not determine whether the latter two coupling constants have the same sign as J_{AB}. If one uses the theoretical formulations developed by Karplus for determining the σ-electron[11] and π-electron[3] contributions to the coupling constants, then an absolute assignment can be made. It would seem reasonable to take J_{BX} as due primarily to σ-electron contribution of the type HCCH which varies from about 0 to $+18$ c.p.s. depending on the angular disposition of the two C—H bonds. The π-electron contribution for a system H—C=C=C—H (J_{AB}) as calculated by Karplus is about -6.7 c.p.s.[3] From the double irradiation experiments reported here we found that J_{AB} has a different sign from J_{BX} which is consistent with Karplus' theoretical work.[3] From our work and that of Snyder and Roberts[1] the relative signs of all the coupling constants can be assigned. Then on the basis of Karplus' theoretical work the signs of J_{AX} and J_{BX} should be positive and the sign of J_{AB} negative.

Acknowledgments.—The authors are indebted to Dr. R. Freeman for information on his use of spin decoupling for the determination of the relative signs of proton–proton coupling constants. We are grateful to Dr. E. I. Snyder and Professor J. D. Roberts for the sample of 1-chlorobutadiene-1,2.

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(9) S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958); **32**, 1700 (1961).

(10) See for example: J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959); C. N. Banwell, A. D. Cohen, N. Sheppard and J. J. Turner, *ibid.*, 266 (1959); R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1959); A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A252**, 488 (1959); F. S. Mortimer, *J. Mol. Spec.*, **3**, 335 (1959); P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **33**, 727 (1960); E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1960); C. N. Banwell and N. Sheppard, *ibid.*, **3**, 351 (1960); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[CONTRIBUTION NO. 2741 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Long-Range Nuclear Spin–Spin Coupling. Allenic and Polyacetylenic Systems[1]

BY EUGENE I. SNYDER[2] AND JOHN D. ROBERTS

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Spin–spin coupling between protons separated by 5 to 9 chemical bonds has been observed in allenic and polyacetylenic systems. Analysis of the n.m.r. spectrum of 1-chloro-1,2-butadiene by various techniques permits assignment of a sign to J_{13} opposite to that of J_{12} and J_{14}. Relation of these results to the theory of proton–proton spin–spin coupling is discussed.

Theoretical studies of the mechanism(s) of nuclear spin–spin coupling constants have been rather successful in elucidating the quantitative aspects of some types of proton–proton spin coupling. In particular, Karplus and co-workers have utilized the groundwork by Ramsey[3] and McConnell[4] to devise means which enable correct predictions of both the magnitude and the sign of several types of proton–proton coupling constants,[5] particularly for unsaturated organic molecules. Recent reports of considerable long-range couplings in saturated systems[6] and of possibly negative 1,2-coupling constants in alkyl derivatives[7] may well diminish the degree of faith with which the Karplus approach may be applied to saturated molecules. The utility for unsaturated systems has so far remained unquestioned.

An advantage of the Karplus approach to spin coupling for organic chemists is the manner in which it permits qualitative conceptualization of the nature of proton–proton spin coupling within the framework of valence-bond theory. Thus, compounds for which valence-bond structures with a hydrogen–hydrogen bond may be written in the manner of "second-order hyperconjugation"[8] can

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(1) Supported in part by the Office of Naval Research.

(2) Postdoctoral Fellow of the Division of Medical Sciences of the United States Public Health Service.

(3) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(4) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

(5) (a) For a summary, see M. Karplus, *ibid.*, **64**, 1793 (1960); (b) M. Karplus, *ibid.*, **33**, 1842 (1960); (c) H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959); (d) M. Karplus, *ibid.*, **30**, 6 (1959); (e) *cf.* also H. Conroy, *Adv. in Org. Chem.*, **2**, 265 (1960).

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