ments 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

RECEIVED OCTOBER 12, 1961

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).

(6) (a) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2770 (1961); (b) D. R. Davis, R. P. Lutz and J. D. Roberts, *ibid.*, **83**, 246 (1961); (c) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **34**, 980 (1961); (d) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (e) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960).

(7) (a) F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4667 (1961); (b) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961); (c) R. R. Frazer, R. U. Lemieux, and J. D. Stevens, *J. Am. Chem. Soc.*, **83**, 3901 (1961).

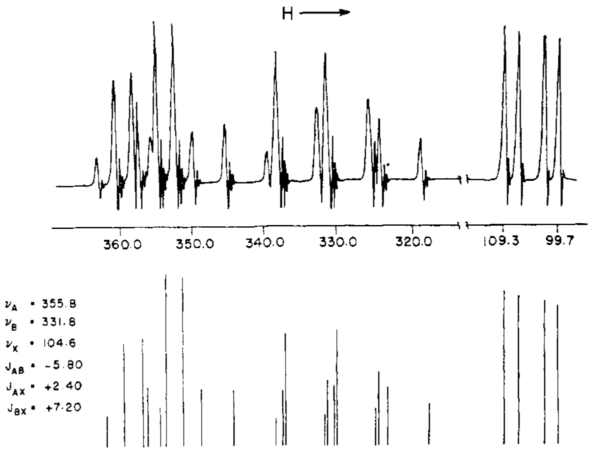

Fig. 1.—Experimental n.m.r. spectrum at 60 mc. for neat 1-chloro-1,2-butadiene (top) and spectrum calculated for the parameters indicated (bottom).

be expected to exhibit at least some degree of spin coupling between the two relevant protons. The predicted magnitude of the coupling constant depends upon the importance of the resonance structures of this type to the over-all resonance hybrid while the sign of the coupling constant is obtained from the algebraic summation of the coupling constants deduced from the individual structures. The coupling constants associated with particular structural features have been in part evaluated from electron–proton hyperfine interactions in paramagnetic resonance studies.

The purposes of the present work were to determine the magnitude and sign of coupling constants in allenic derivatives and to investigate some unsaturated systems for which significant "super long-range" coupling constants might reasonably be expected.

Results

The coupling constants found for the various compounds which were investigated are summarized in Table I. Coupling constants between equivalent protons and between the accidentally equivalent acetylenic and methyl protons in 1,3-pentadiyne were obtained from the ^{13}C-satellite spectra.[9] All of the coupling constants except those for 1-chloro-1,2-butadiene could be obtained by simple first-order interpretation of the relevant spectra.

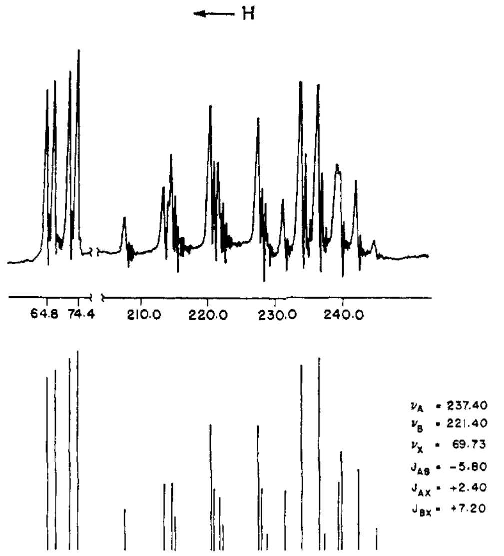

Fig. 2.—Experimental n.m.r. spectrum at 40 mc. for neat 1-chloro-1,2-butadiene (top) and spectrum calculated for the parameters indicated (bottom).

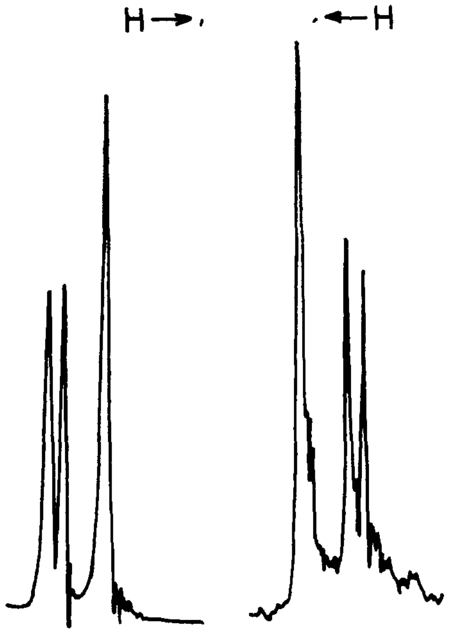

Fig. 3.—Methyl group pattern observed in double-resonance experiments with sideband of 258 c.p.s. (left) and 245 c.p.s. (right).

The coupling and chemical shift parameters for 1-chloro-1,2-butadiene, an ABX_3 system, were obtained in the following manner. The relative sign of J_{AX} and J_{BX} was determined from the behavior of the X_3 resonance signals at 40 and 60 mc., for the theory of ABX_3 systems demands that those lines whose separation is $|J_{AX} + J_{BX}|$ be field invariant.[10] From Figs. 1 and 2 it is apparent that $|J_{AX} + J_{BX}| = 9.6$ c.p.s. Since the data from other allenes and alkenes possessing the $CH_3CH{=}$ grouping indicate that J_{AX} and J_{BX} should be about 2–3 and 7 c.p.s., respectively, the value of $|J_{AX} + J_{BX}|$ implies that both coupling constants are of the same sign. Further support for this assignment is given by the outward movement of the inner X_3 lines with increasing magnetic field, behavior which is characteristic of an ABX_3 system when $|J_{AX} + J_{BX}| > |J_{AX} - J_{BX}|$.[10] That the sign of J_{AB} is opposite to that of J_{AX} was unequivocally established from double-resonance experiments of the type described by Freeman,[11] performed for us by Drs. Dan Elleman and S. L. Manatt of the Jet Propulsion Laboratory.

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[8] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 150–152.

[9] A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

[10] V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **33**, 1794 (1960).

[11] R. Freeman, *Mol. Phys.*, **3**, 435 (1960); R. Freeman and D. H. Whiffen, *ibid.*, **4**, 321 (1961); R. Freeman, *ibid.*, **4**, 385 (1961). See also J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 208 (1961).

TABLE I

COUPLING CONSTANTS IN SOME UNSATURATED SYSTEMS

Compound	Solvent	J_{H-H}, c.p.s.	$J_{^{13}C-H}$, c.p.s.
$(CH_3)_2C{=}C{=}CH_2$	Neat	$J_{14} = 3.03 \pm 0.06$	166[a]
$(CH_3)_2C{=}C{=}CHCl$	Neat	$J_{14} = 2.14 \pm .08$	
$CH_3CH{=}C{=}CHCl$	Neat	$J_{AB} = J_{13} = \mp 5.8 \pm 0.1$	
X_3 B A			
		$J_{AX} = J_{14} = \pm 2.4 \pm 0.1$	
		$J_{BX} = J_{12} = \pm 7.2 \pm 0.1$	
$HC{\equiv}CH$		$J_{12} = 9.1$[b]	
$CH_3C{\equiv}CH$		$J_{13} = 2.9-3.6$[c]	
$CH_3C{\equiv}CCH_3$		2.7[d]	
$HC{\equiv}CC{\equiv}CH$	Neat	$J_{14} = 2.2 \pm 0.2$	259.4
$CH_3C{\equiv}CC{\equiv}CH$	Neat	$J_{15} = 1.27 \pm .05$	132[e]
$CH_3C{\equiv}CC{\equiv}CCH_3$	CCl_4	$J_{16} = 1.3 \pm .1$	132
$ClCH_2C{\equiv}CC{\equiv}CCH_2Cl$	Neat	$J_{16} = 1.0 \pm .2$	158
$CH_3C{\equiv}CC{\equiv}CC{\equiv}CCH_2OH$	CH_3OH	$J_{18} = 0.4$	

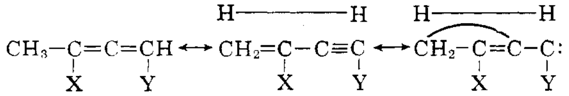
[a] For CH_2 grouping. [b] M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957). [c] J. N. Shoolery, L. F. Johnson and W. A. Anderson, *J. Mol. Spectros.*, **5**, 110 (1960); E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959); W. R. Vaughan and R. C. Taylor, *J. Chem. Phys.*, **31**, 1425 (1959). [d] N. Muller and D. E. Pritchard, *ibid.*, **31**, 768 (1954). [e] For CH_3 grouping.

Final values of the n.m.r. parameters were obtained by an iterative procedure, based on an exact solution of the high resolution n.m.r. Hamiltonian, programmed for an IBM 7090 computer. Calculated and experimental spectra for both 40 and 60 mc. are shown in Figs. 1 and 2.

The extreme ease of polymerization of butatriene[12] even at −28° thwarted our attempts to record the ^{13}C-satellites of its proton spectrum. This was unfortunate since comparison of the experimental and predicted[5b] value would have been particularly interesting.

Discussion

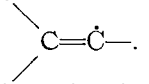
The spectra of the allenic compounds examined clearly demonstrate the existence of a 1,4-coupling constant (J_{14}) of magnitude 2–3 c.p.s. Assuming that J_{12} is positive, as theory predicts,[5c,d,13] then J_{14} is positive and the coupling constant between the allenic protons (J_{13}) is negative. Our results thus provide experimental verification of Karplus' prediction[5b] of a negative sign for this latter type (J_{13}) of coupling constant. No theoretical considerations regarding either the sign or magnitude of J_{14} in allenic systems are available. If one assumes that for compounds of type I that Ia is an important valence-bond structure from the standpoint of proton–proton coupling, then J_{14} is predicted to be positive.[5b] However, the magnitude of J_{14} so calculated, 3.9 c.p.s., is rather larger than the experimental value (3.0 c.p.s.). This discrepancy suggests that perhaps structure Ib, with a predicted negative J_{14}, is sufficiently important (in the spin–spin coupling sense) to reduce substantially the coupling below the calculated value.



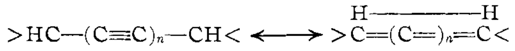
$$\underset{\text{I}}{CH_3-\underset{X}{C}=C=\underset{Y}{CH}} \longleftrightarrow \underset{\text{Ia}}{CH_2=\underset{X}{C}-C\equiv\underset{Y}{C}} \longleftrightarrow \underset{\text{Ib}}{CH_2-\underset{X}{C}=C-\underset{Y}{C}:}$$

I Ia Ib

A necessary corollary of this would be that a significant hyperfine interaction is associated with the structural grouping CH$_3$



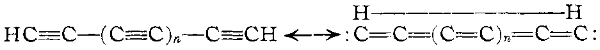
Consideration of the valence bond structures of dialkyl-substituted polyacetylenes of type II suggests that these systems should exhibit long-range couplings.



$$>HC-(C\equiv C)_n-CH< \longleftrightarrow >C=(C=)_n=C<$$

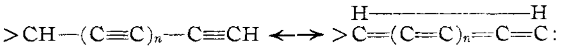
II IIa

Similarly, the simple and monoalkyl-substituted polyacetylenes (III and IV) groupings might also exhibit substantial long-range coupling.



$$HC\equiv C-(C\equiv C)_n-C\equiv CH \longleftrightarrow :C=C=(C=C)_n=C=C:$$

III IIIa



$$>CH-(C\equiv C)_n-C\equiv CH \longleftrightarrow >C=(C=C)_n=C=C:$$

IV IVa

The first members of series II ($n = 1$) and IV ($n = 0$) are known to have their terminal protons spin-coupled (see Table I). We have prepared several representatives of series II ($n = 2,3$) and have demonstrated coupling across 7 and 9 bonds, respectively (*cf.* Table I). The terminal protons are also coupled in those representatives of series III ($n = 0$) and IV ($n = 2$) examined by us.

Comparison of the J-values for acetylenes is illuminating in several respects. Firstly, were a direct-through-space mechanism *the* important one for proton–proton coupling, $|J|$ would be inversely proportional to the third power of the distance between protons and would decrease with n much faster than it actually does. The inapplicability of direct mechanisms to *proton–proton* spin coupling has been frequently cited on theoretical bases,[3,4,5b] and the present series of compounds provides a (probably unnecessary) experimental confirmation of the unimportance of such mechanisms.

Hoffman and Gronowitz have predicted[14] that

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[12] W. M. Schubert, T. H. Liddicoet and W. A. Lanka, *J. Am. Chem. Soc.*, **76**, 1929 (1954).

[13] Note, however, that recent work[7a] strongly suggests that J_{AB} is indeed of opposite sign to J_{AX} and J_{BX} in diethyl sulfite. Consequently, either 1,1- or 1,2-couplings seem to be required to be negative in saturated compounds.

[14] (a) R. A. Hoffman, *J. Mol. Phys.*, **1**, 326 (1958); (b) R. A. Hoffman and S. Gronowitz, *Acta Chem. Scand.*, **13**, 1477 (1959).

substitution of a methyl group for an olefinic proton should give essentially the same coupling between some other proton and the methyl group as between the other proton and the olefinic proton, provided that coupling is transmitted by a π-electron system. The rationale of this suggestion is that the hyperfine interaction constant for methyl and ethyl radical fragments are nearly identical in magnitude although opposite in sign.[14a,15] The same approach does not seem to apply to the acetylenic series, where substitution of a hydrogen by a methyl group in diacetylene causes considerable decrease in $|J|$, perhaps because of the lack of a similar relation between the hyperfine interaction constants of higher radical fragments, *e.g.*, $HC{\equiv}C\text{–}\dot{C}$ and $CH_3C{\equiv}C\text{—}\dot{C}$. It is possible, if the current theory[5b] of spin coupling in π-electron systems is valid, that the magnitude of appreciable hyperfine interactions in radicals of this type might be more easily evaluated from n.m.r. than e.p.r. spectra.

One point may be of practical importance to the organic chemist who uses nuclear magnetic resonance spectroscopy as a tool for analysis of organic structures. Although the concept of conjugation is highly useful for ultraviolet and infrared spectroscopy, uninhibited extension of the concept to qualitative considerations of spin coupling constants may be misleading. By way of illustration, J_{14} in the conjugated system, diacetylene, is less than that in butyne-2. Furthermore, J_{14} in 1-chloro-1,2-butadiene, where each double bond behaves as an independent unit, is easily observable, and larger than in some conjugated systems,[16] whereas J_{14} in 3-chloro-1-butyne is not observable. The mere existence or absence of a conjugated system is not enough and one must consider first of all those valence-bond structures to which can be ascribed the origin of spin-coupling constants. Caution must be exercised here also, because contributions from various structures can both reinforce or cancel one another.

Since hyperconjugation appears to be almost inextricably bound to the theoretical development of the phenomenon of proton–proton spin–spin coupling,[14] it might be worthwhile to mention that ground-state hyperconjugation can be regarded as highly important for spin–spin coupling even though it is almost certainly relatively unimportant so far as determining the energy of the ground state is concerned.[17] It remains to be seen how well spin-coupling constants, as a measure of hyperconjugation (or some similar electronic effect), can be used for correlation of changes in rate or equilibrium constants due to substituent groups.

Experimental

Nuclear magnetic resonance spectra were recorded with a Varian Associates high resolution n.m.r. spectrometer operated at 60 mc., unless otherwise noted, and equipped with a Super Stabilizer. Line positions relative to a suitable internal standard were measured by either the sideband superposition technique or by interpolation between sidebands placed laterally to the resonance signals.

3-Methyl-1,2-butadiene was prepared by lithium aluminum hydride reduction of 3-chloro-3-methyl-1-butyne[18] and purified by distillation through a Nestor-type spinning-band column followed by redistillation of the fractions of >94% purity ($n^{20}_{\rm D}$ 1.4116–1.4190) through a center-tube fractionating column. A fraction, b.p. 39–40°, $n^{20}_{\rm D}$ 1.4188 (lit.[18] b.p. 40.0–40.2°, $n^{25}_{\rm D}$ 1.4148), of 99^{+}% purity (by v.p.c. analysis on a diisodecyl phthalate column) was used for the spectral work.

1-Chloro-3-methyl-1,2-butadiene.—Omission of copper bronze from the published procedure[19] for preparation of this compound resulted in no deleterious effects, and 57% of crude product of b.p. 40–50° (105–92 mm.), $n^{25}_{\rm D}$ 1.4662–1.4741, was obtained. Careful fractionation through a Nestor-type spinning-band column of a high-boiling cut, $n^{25}_{\rm D}$ 1.4741, gave a sample of b.p. 51.8–52.0° (110 mm.), $n^{25}_{\rm D}$ 1.4744 [lit.[19] b.p. 60–63° (175 mm.), $n^{25}_{\rm D}$ 1.4740], 99.5% pure by v.p.c., which was used for the spectral work.

1-Chloro-1,2-butadiene.—Treatment of 3-butyn-2-ol with thionyl chloride in diethyl Carbitol afforded a mixture of 1-chloro-1,2-butadiene and 3-chloro-1-butyne.[20] The allene was separated by preparative v.p.c.[21] and was 99.7% pure by v.p.c. 3-Chloro-1-butyne was the major component of the reaction mixture and when separated had $n^{25}_{\rm D}$ 1.4214.

Anal. *Calcd.* for C_4H_5Cl: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 53.93; H, 5.86; Cl, 39.64.

An attempt to prepare 1-bromo-1,2-butadiene by an SN2′ displacement with lithium bromide on the tosylate of 3-butyn-2-ol afforded only the acetylenic bromide.

Diacetylene generated from 1,4-dichloro-2-butyne-2[22] was purified by sublimation at −30° followed by a bulb - to-bulb distillation. A sample was sealed into an n.m.r. tube at 1 mm. and stored at −78°. Spectra were recorded at the ambient temperature (~28°).

1,3-Pentadiyne.—An explosion occurred in an attempt to prepare this compound by the method of Armitage and co-workers.[23] Accordingly, the isolation procedure was modified slightly. The material obtained by concentration of the butane extract of the reaction mixture was filtered and distilled at water-pump pressure. The distillate was collected at −78° and then rapidly distilled on a steam-bath in an atmosphere of prepurified nitrogen to afford 1,3-pentadiyne in two fractions, $n^{20}_{\rm D}$ 1.4762, 1.4770 (lit. $n^{15}_{\rm D}$ 1.4790,[24] 1.4717[23]). Extensive decomposition was found to accompany distillation. A portion of the product was distilled under reduced pressure into an n.m.r. tube containing benzene and stored *in vacuo* in the dark at −78° until its spectrum was recorded at room temperature.

2,4-Hexadiyne.—The reported procedure afforded material of m.p. 65.0–65.8° (sealed capillary, lit.[22] m.p. 67°). Its n.m.r. spectrum was determined for a 50% solution in carbon tetrachloride.

1,6-Dichloro-2,4-hexadiyne.—Treatment of 2,4-hexadiyne-1,6-diol[22] in pyridine with thionyl chloride afforded yellowish dichloride of b.p. 55–58° (0.5 mm.), $n^{20}_{\rm D}$ 1.5749 [lit.[25] b.p. 61° (0.5 mm.), $n^{16}_{\rm D}$ 1.5770]. The product was stored at 0° prior to spectroscopic investigation.

2,4,6-Octatriyn-1-ol was prepared from bromopropargyl alcohol and 1,3-pentadiyne as described by Chodkiewicz.[26] Two recrystallizations in the dark from carbon tetrachloride gave material of m.p. 92–93° (lit.[27] m.p. 93°). Because of

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(15) For a summary and references, see R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 471 (1960).

(16) E. I. Snyder, unpublished work.

(17) The ground state energy of methane is supposedly changed by only 1.3 kcal. by inclusion of those structures responsible for spin coupling (ref. 3d).

(18) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

(19) G. F. Hennion, J. J. Sheehan and D. E. Maloney, *J. Am. Chem. Soc.*, **72**, 3542 (1950).

(20) T. L. Jacobs, W. L. Petty and E. G. Teach, *ibid.*, **82**, 4094 (1960).

(21) We wish to thank Mr. Kent Smitheman of American Potash Co. for performing this separation.

(22) J. B. Armitage, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 44 (1951).

(23) J. B. Armitage, E. R. H. Jones and M. C. Whiting, *ibid.*, 1993 (1952).

(24) H. Schlubach and V. Wolf, *Ann.*, **568**, 141 (1950).

(25) C. L. Cook, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 2883 (1952).

(26) W. Chodkiewicz, *Ann. chim.*, [13] **2**, 852 (1957).

the extreme photosensitivity and the line-broadening effect of the photolysis products on the n.m.r. spectrum, a sample was sublimed in the dark at 0.5 mm. immediately prior to spectral study. The resulting material was pure white; it was dissolved in methanol, stored at 0°, and protected from light.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Reduction of Unsaturated Compounds by Ammoniacal Chromium(II)

BY KENNETH D. KOPPLE

RECEIVED OCTOBER 25, 1961

Chromium(II) in concentrated aqueous ammonia has been shown to convert benzaldehyde and acetophenone to carbinols and to saturate the ethylenic double bond of cinnamic acid and mesityl oxide. Differences between this reagent and aquo chromium(II) are discussed.

Chromium(II), while stable in oxygen-free aqueous acid, has been observed to evolve hydrogen from alkaline solutions containing excess oligopolyethylenimines.[1] This observation suggested that it might be worthwhile to establish how other reducing properties of chromium(II) ammines differ from those of the aquo ion. Almost 100 years ago Berthelot reported that ammoniacal chromium(II) chloride converted acetylene to ethylene,[2] but with the exception of some experiments with chromium(II) hydroxide[3] subsequent studies of the action of divalent chromium on unsaturation have been limited to reaction in acidic solution.

Solutions of chromium(II) ion in concentrated aqueous ammonia may be stored under nitrogen for weeks without apparent decomposition, but they react almost instantaneously with a number of α,β-unsaturated carbonyl compounds that are unaffected by acidic solutions of chromium(II) salts. In their survey of the reactivity of the latter solutions toward carbonyl compounds,[4] Conant and Cutter found that while acetylenic derivatives, quinones and maleic and fumaric acids underwent two-electron reduction, where reaction occurred with other α,β-unsaturated carbonyl compounds one-electron products were obtained. For example, benzaldehyde and other aromatic aldehydes were converted to hydrobenzoins. (Acetophenone and saturated aliphatic aldehydes were not attacked.) Acrolein was reduced to 3,4-dihydroxy-1,5-hexadiene and benzalacetone to 4,5-diphenyl-2,7-octadione. (Mesityl oxide and cinnamic acid resisted attack.) In contrast, ammoniacal chromium(II) sulfate affords, upon extraction of the reaction mixture, two-electron products from benzaldehyde (benzylamine, isolated in 31% yield as the N-phenylurea), acetophenone (α-phenylethyl alcohol, isolated in 71% yield as the N-phenylcarbamate), mesityl oxide (methyl isobutyl ketone, isolated in 33% yield as the 2,4-dinitrophenylhydrazone) and cinnamic acid (hydrocinnamic acid, isolated in 45% yield). A related example, the reduction of cinnamic to hydrocinnamic acid by chromium(II) hydroxide, has been reported.[3] Other substances, not affected by the acidic solutions, that rapidly oxidize the ammoniacal reagent include acrylonitrile, acrylic acid and acrylamide. Neither reagent affects aliphatic ketones or cinnamyl alcohol.

When reaction occurs with the ammoniacal reagent, it is rapid and, where excess oxident is used, chromium(II) is consumed completely. Low yields of isolated product occur because of the formation of stable, unextractable chromium(III) complexes of the organic products. (A quantity of organic-soluble complex of hydrocinnamic acid was obtained; on decomposition it afforded an additional 17% of the acid.) Conant and Cutter apparently had the same difficulty with acidic chromium(II); they obtained cleaner organic products when vanadium(II) was used.

Experimental

Materials and Methods.—For reduction experiments on a preparative scale a 0.8 *M* solution of chromium(II) sulfate in 1.2 *N* sulfuric acid, obtained by zinc reduction of a chromium(III) sulfate solution, was employed. This was stored in a serum-capped flask, under nitrogen, and transferred by means of a hypodermic syringe to reaction vessels which were likewise capped. The contents of these flasks had been freed of air by flushing with nitrogen before addition of the reductant.

For other experiments a stable solution of chromium(II) chloride in concentrated aqueous ammonia was prepared by solution of the anhydrous salt in concentrated aqueous ammonia. Screening experiments were carried out in serum-capped test-tubes using this reagent. The occurrence of reaction was assumed to be indicated by a color change from deep blue to orange or violet.

Spectra were measured by means of a Cary model 14 spectrophotometer. Ammoniacal chromium(II) chloride was added to a serum-capped test-tube containing an excess of the pure oxidant. After reaction had occurred, the tube was immersed in a Dry Ice–acetone-bath until the contents were frozen and then mixed with sufficient 6 *N* HCl to give 1–2 *M* excess hydrogen ion. When an oxygen-free atmosphere was required the thawed contents of the reaction tubes were transferred by syringe to serum-capped, nitrogen-flushed cuvettes for measurement.

Substances Screened.—The following substances, used in excess, reacted within seconds with ammoniacal chromium(II) chloride or sulfate: cinnamic acid, maleic acid, acrylic acid, acrylamide, acrylonitrile, benzaldehyde, acetophenone, mesityl oxide, *p*-benzoquinone. Unreactive on 24-hr. storage with the reagent were cinnamyl alcohol, hexamethylenetetramine, methyl ethyl ketone, diethyl ketone, phenetole.

In one experiment 0.5 ml. of freshly distilled acrylonitrile was shaken, under nitrogen, with 4 ml. of 0.1 *M* chromium(II) chloride in concentrated ammonia. The clear orange solution which resulted gradually reddened, and after 24 hr. was reddish-violet and still free of precipitate. It was acidified and dialyzed against water. Material remaining in the

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(1) K. D. Kopple, G. F. Svatos and H. Taube, *Nature*, **189**, 393 (1961).

(2) M. Berthelot, *Ann. chim.*, [4] **9**, 401 (1866).

(3) W. Traube and W. Passarge, *Ber.*, **49**, 1692 (1916).

(4) J. B. Conant and H. Cutter, *J. Am. Chem. Soc.*, **48**, 1016 (1926).