The Formation of Phthaloyl Phosphate. A series of solutions, 0.05 *M* in total phosphate and varying from pH 5.05 to 7.56, were prepared; 3-ml of the respective phosphate solution was injected into 10 ml of a 3% solution of phthalic anhydride in dioxane, and the change in anhydride concentration with respect to time was followed in a thermostated Cary 11 system.

The Hydrolysis of Phthaloyl Phosphate. The reaction was followed by two different methods. The solutions were prepared by injecting 1 ml of a 2% phthalic anhydride solution in dioxane into 100 ml of phosphate buffer of ionic strength 1.5. At pH values below 7.5, calculated amounts of K_2HPO_4, NaH_2PO_4, and NaCl were weighed out on an analytical balance to give the desired phosphate ratio and an ionic strength of 1.5. At pH values greater than 7.5, the phthaloyl phosphate was prepared by injecting into 100 ml of Na_2HPO_4 solution of the desired concentration and then adding solid sodium hydroxide to the ionic strength of 1.5 based on phosphate being totally in the diionic form. The reaction was then followed directly on the Cary 11 at 290 mμ or indirectly by quantitatively regenerating phthalic anhydride by injecting 2.6 ml of solution into 0.5 ml of concentrated HCl. The former method was used at low pH values where the reaction was relatively fast; the latter was used at high pH values to avoid waiting for an equilibrium value. In the indirect technique the amount of anhydride produced in any sampling was directly proportional to $A_0 - A_\infty$ at 302 mμ. The A_0 value was obtained by extrapolating back to the injection time as seen on the Cary chart. In all cases the pH of the reaction mixture was measured after the anhydride had been added.

The Formation of Phthalic Anhydride from Phthaloyl Phosphate. The method consisted of a slight modification of the direct technique for following phthaloyl phosphate hydrolysis as described above. Acetic acid solutions of varying strength were used instead of hydrochloric acid solutions. A 2.6-ml portion of phosphate solution containing phthaloyl phosphate was injected into 0.5 ml of acetic acid of varying concentrations. The appearance of phthalic anhydride was followed at 302 mμ. After completion of the reaction, the pH of the solution in the cell was measured with microelectrodes.

Mechanisms of Nucleophilic Substitution of Propargyl and Allenyl Halides. Base-Promoted Reactions of 3-Bromo-3-methyl-1-butyne and 1-Bromo-3-methyl-1,2-butadiene in Aqueous Ethanol[1]

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Contribution No. 1421 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received April 18, 1966*

Abstract: Evidence is presented which shows that both the propargyl and the allenyl bromides (Ib and IIb) react with aqueous alcoholic base by rapid, reversible removal of the terminal proton followed by rate-determining loss of the halide ion and formation of the same allene–carbene intermediate. Although this species is attacked by lyate ions to form only propargyl products, its reaction with added thiophenoxide or azide ions gives both acetylene and allene derivatives. Proton magnetic resonance spectra indicated that the propargyl and allenyl azides initially formed subsequently reacted *in situ* to produce other materials. Salt effects and solvent and reactant secondary deuterium isotope effects have been used to elucidate some of the mechanistic details, and a tentative hypothesis is offered to explain why different nucleophiles give such widely differing acetylene/allene product ratios.

In 1951 Hennion and Maloney[2] proposed that the second-order base-promoted solvolysis of 3-chloro-3-methyl-1-butyne (Ia) and the isomeric allenyl halide, 1-chloro-3-methyl-1,2-butadiene (IIa), involved as a common intermediate the propargyl zwitterion–allene carbene species, III. The suggested mechanism was essentially that shown in Figure 1 with the slow step in each case being the formation of the conjugate bases in steps 1 and 2.

In 1952 Shiner and Wilson[3] offered conclusive kinetic evidence for the intermediacy of the species III in the solvolysis of the propargyl halides Ia and Ib in basic aqueous ethanol. They showed that Ib exchanged the acetylenic hydrogen in basic 80% ethanol-*d*–deuterium oxide solution much faster than it solvolyzed and that the rate of the second-order solvolysis in the nondeuterated medium was depressed by added sodium salts in the order: $Br^- > Cl^- > NO_3^- \sim ClO_4^-$. These results are consistent with the Hennion mechanism only if the rate-determining step is the ionization of bromide from the conjugate base of Ib, step 3 in Figure 1.

Gas chromatographic analyses of distillates from the reaction mixture of Ib in basic aqueous ethanol indicated that the propargyl ether VI was the predominant product (90% *relative* yield) accompanied by only small amounts of the propargyl alcohol V (7%) and volatile olefin IV (3%).[3] In comparison, the first-order, initially neutral solvolysis of Ib, characterized as an SN1 process,[3,4] yielded an entirely different distribution of these same propargyl products: VI, 43%; V, 22%; and IV, 35%.[3] "The difference in product proportions is apparently dictated by the different reactivity, and therefore selectivity, of the two intermediates, the carbonium ion and the zwitterion–carbene.

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[1] (a) Taken from the thesis submitted by J. S. Humphrey, Jr., to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree, 1965. (b) Presented in part before the Division of Organic Chemistry at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. (c) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] G. F. Hennion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951).

[3] V. J. Shiner, Jr., and J. W. Wilson, *ibid.*, **84**, 2402 (1962).

[4] V. J. Shiner, Jr., J. W. Wilson, G. Heinemann, and N. Solliday, *ibid.*, **84**, 2408 (1962).

The latter is more stable and more selective because the allene–carbene resonance-contribution form IIIb contains no formal charges and therefore contributes more importantly to the structure III than the allene carbonium ion VIIb does to the structure VII."[3] Since the

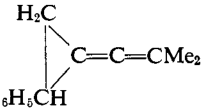
$$[\underset{a}{Me_2\overset{+}{C}C\equiv CH} \underset{VII}{\longleftrightarrow} \underset{b}{Me_2C=C=\overset{+}{C}H}]$$

acetylide group, $-C\equiv C:^-$, is more effective than the acetylene group, $-C\equiv CH$, in stabilizing the incipient positive charge at the propargyl carbon atom, the demand for hyperconjugative stabilization by the adjacent methyl groups is less in the transition state leading to III of the second-order process than in that leading to VII of the first-order process. Thus the observation of a much smaller secondary isotope effect on the base-promoted reaction (k_H/k_{D_6} = 1.31) than in the carbonium ion reaction (k_H/k_{D_6} = 1.84) could be explained.

Recent volumes of activation measurements for the base-promoted reaction of the propargyl chloride Ia have been successfully interpreted in terms of the intermediate III, and it was further suggested that canonical forms analogous to IIIa and IIIb contributed approximately equal weight in the transition-state structure.[5]

An attempt to trap the intermediate III with sodium azide was inconclusive because a competing second-order reaction between the azide and propargyl bromide (Ib) prevented an unambiguous demonstration of the occurrence of III in this process.[3] Further, the products of the reaction with azide ion could not be identified.

Under nonsolvolytic conditions, the reactions of Ia and IIa with styrene solvent are effected by potassium *t*-butoxide, and each substrate yields the same alkenylidenecyclopropane, VIII.[6a,c] Further evidence for the formation and high electrophilicity of III in an olefin medium in the absence of other nucleophilic reagents is the fact that the rate of addition increases with increasing substitution of the alkene link and proceeds stereospecifically with *cis*- and *trans*-2-butene.[6b,c]



VIII

Most of the information regarding the existence and nature of III has thus centered upon the reactions involving tertiary propargyl halides. Other than the original work of Hennion and Maloney and the trapping experiments of Hartzler, no further evidence regarding the mechanism of the base-promoted solvolyses of *allenyl* halides has been presented. The possibility that SN2 and SN2′ types of reaction might occur with these reactants must be entertained. If III is an intermediate in the allene reaction, is it generated from the allene halides by a *concerted* α-elimination path in analogy to the base-promoted decomposition of some fluorine-containing haloforms[7] or does the two-step Hennion mechanism obtain? Of further interest is a definitive product assay which demonstrates whether or not III gives rise to any allene derivatives.

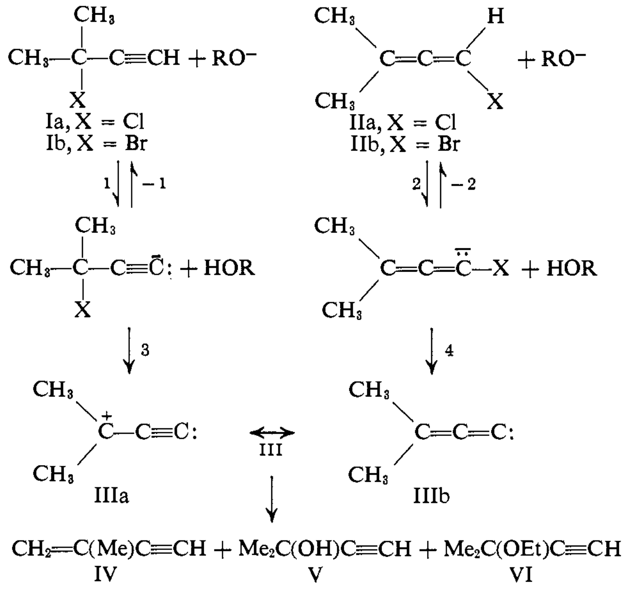


Figure 1. Reaction scheme for the base-promoted solvolyses of isomeric allenyl and tertiary propargyl halides.

Methods and Results

Products of the Second-Order Reactions of Ib and IIb in Basic Aqueous Ethanol. A quantitative proton magnetic resonance (pmr) study has been carried out for the products formed in the solvolysis reactions of Ib and IIb in the presence of a slight excess of sodium hydroxide in 70, 80, and 90 vol. % aqueous ethan-2,2,2-d_3-ol (0.58, 0.45, and 0.27 mole fraction of water, respectively). The methyl resonances of Ib, IIb, IV, V, and VI are easily distinguished in the δ 1–2 region: Ib, δ 2.00, singlet; IIb, δ 1.84, doublet (J = 2.5 cps); IV, δ 1.90, complex multiplet; V, δ 1.45, singlet; and VI, δ 1.42, singlet [relative to tetramethylsilane (TMS) in 80% aqueous ethanol]. The isotopic impurity of the solvent provided a convenient internal standard to compare integral measurements; thus it could be shown that within the sensitivity of the method the three propargyl derivatives (IV, V, and VI) quantitatively account for the consumption of Ib and IIb. The yields quoted in Table I, which summarizes the results, are therefore

Table I. Products of the Basic Solvolyses of 3-Bromo-3-methyl-1-butyne (Ib)[a] and 1-Bromo-3-methyl-1,2-butadiene (IIb) in 70, 80, and 90 Vol. % Aqueous Ethan-2,2,2-d_3-ol as Determined by Pmr[b]

Solvent, %	Substrate (*m*)	Base, *m*	Mole %[c] olefin (IV)	Propargyl alcohol (V)[d]	Ether (VI)[d]
70	Ib (0.59)	0.61	13[d]	19	68
	IIb (0.62)	0.67	9	21	70
80	Ib (0.71)	0.76	13[d]	13	74
	IIb (0.72)	0.72	14	14	72
90	Ib (0.72)	0.77	16[d]	8	76
	IIb (0.84)	0.84	13	8	79

[a] In the earlier work[3] a drastic fall-off in the integrated second-order rate constants near the end of the solvolysis of Ib in basic aqueous ethanol was attributed to the formation of some of the less reactive IIb during the course of the reaction by isomeric external return of the bromide ion. In the present work this conclusion is confirmed by the appearance of the signals of a few per cent of IIb in the pmr spectrum during the course of the reaction. [b] Ambient probe temperature, 30°. [c] Estimated accuracy = ±3–4%. [d] See the Experimental Section.

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(5) W. J. le Noble, *J. Am. Chem. Soc.*, **87**, 2434 (1965).

(6) (a) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961); (b) *ibid.*, **83**, 4997 (1961); (c) *J. Org. Chem.*, **29**, 1311 (1964).

(7) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957).

on an absolute basis. They differ somewhat from those previously reported,[3] but the earlier conclusions are unaffected; the disparity in the results may be due in part to the higher concentration of reactants in the present experiments but probably also reflects the superiority of the nmr technique for product analyses.[8]

Reactions of Ib and IIb with Sodium Thiophenoxide. The products of these reactions in deuterium oxide solutions of ethan-2,2,2-d_3-ol-d (both in the presence and absence of added excess sodium hydroxide) have been determined by integration of the pmr signals of the crude reaction mixtures. The results are summarized in Table II. The enyne IV, the propargyl ethyl ether VI, the propargyl phenyl sulfide IX, and the allenyl phenyl sulfide X within about 5% experimental error account for all of the reacted material. The recorded exchange and reaction times are estimates based on peak height measurements. The comparison of reactions 1 with 3 and 2 with 4 (Table II) indicate that the reaction and terminal proton exchanges of both Ib and IIb are markedly accelerated by excess base. Thus the products of reactions 3 and 4 result from trapping an intermediate generated by base and do not come from direct nucleophilic displacement. The results show that the products and yields in the base-promoted reactions of the allenyl bromide and propargyl bromide are identical within experimental error. Further, the yields in these reactions are different from those of either bromide reacting with thiophenoxide in the absence of excess base as shown in reactions 1 and 2 (Table II).

Table II. Pmr Analysis of Reactions of 3-Bromo-3-methyl-1-butyne (Ib) and 1-Bromo-3-methyl-1,2-butadiene (IIb) with Sodium Thiophenoxide in Aqueous Ethanol[a,b]

Reaction no.	1	2	3	4	5
Mole fraction of D_2O	0.41	0.44	0.48	0.45	0.49
Molality of reactants					
$Me_2CBrC{\equiv}CH$ (Ib)	0.31	. . .	0.31	. . .	0.30
$Me_2C{=}C{=}CHBr$ (IIb)	. . .	0.30	. . .	0.30	. . .
$NaSC_6H_5$	0.89	0.89	0.91	0.92	0.58
NaOD	0	0	0.94	0.92	1.04
Product proportions in mole %			*d*		
$CH_2{=}C(Me)C{\equiv}CH$ (IV)	10	0	10	7	*g*
$Me_2C(OEt)C{\equiv}CH$ (VI)	0	0	9	9	15
$Me_2C(SC_6H_5)C{\equiv}CH$ (IX)	0	45	50[c]	52[c]	52
$Me_2C{=}C{=}CHSC_6H_5$ (X)	90	55	31	32	33
Approx half-life of product formation, min	2.5	180	0.3	9.5	*f*
Approx half-life for active H exchange, min	2.5	∞	*e*	1	*e*

[a] $CD_3CH_2OD{-}D_2O$ medium. [b] Probe temperature, 30°. [c] Uncorrected for small amounts of $Me_2C(OH)C{\equiv}CH$ present. [d] A small amount of IIb appeared as a reaction intermediate. [e] Exchange so rapid that acetylenic hydrogen not observed. [f] Not estimated, but apparently as fast as reaction 3. [g] Under the conditions of the reaction, the very small amount of IV could not be quantitatively assessed; thus the other entries of the product proportions column are *relative* yields.

Reactions of Ib and IIb with Sodium Azide. Pmr spectral evidence has been obtained for the reactions of Ib and IIb with sodium azide in the presence and absence of strong base in aqueous ethanol. Complications arise in attempting to interpret these spectra, because side reactions consume the presumed initially formed simple azides. Nevertheless, several clear conclusions can be drawn from comparisons of the spectra obtained in these experiments. First, the presence of strong base accelerates the reaction of azide ion with both substrates. Secondly, these comparisons also reveal that the direct reactions (no added lyate ions) of either Ib or IIb with azide ion have different product distributions than are observed in the presence of added base. Thirdly, *the azide reactions carried out in the presence of added base give rise to the same product distributions regardless which bromide reacts,* the only difference being that the longer reaction time for the less reactive allenyl bromide allows the subsequent side reactions to become evident before the substrate is consumed.

We assume that the metastable peaks which were observed at δ 1.47 and 1.63 are due to the methyl resonances of the simple substitution derivatives, $Me_2C(N_3)C{\equiv}CH$ (XI) and $Me_2C{=}C{=}CHN_3$ (XII), respectively, the assigned order having the same positional relationship observed for the bromide and thioether derivatives. Several attempts to isolate these initially formed products on a preparative scale with short reaction times were unsuccessful; the products of further reaction, showing absorptions at δ 1.58 and 2.08, could not be decisively characterized, either.

The identification of the propargyl azide XI appears to be established by the results for the reaction of Ib with hydrazoic acid in deuterium oxide–acetone-d_6. Under these acidic conditions the azide would be formed *via* the carbonium ion, *without* the acetylenic hydrogen being exchanged for deuterium. The acetylenic-type hydrogen absorption at δ 2.78 under these conditions is associated with the methyl resonance at δ 1.45; these absorptions are not due to the propargyl alcohol V, which shows peaks at δ 2.82 and 1.49, respectively, in aqueous acetone.

Reactions of Ib and IIb with Sodium Acetate in Basic Aqueous Ethanol. Acetate ion has been shown to be insufficiently basic to promote the second-order reaction of the propargyl bromide Ib in aqueous ethanol.[3] It was of interest with respect to this observation and the results for the azide trapping experiments described above to ascertain whether acetate ion was nucleophilic enough to be incorporated into the products of the second-order reactions of Ib and IIb in basic aqueous ethanol. When slightly less than 1 equiv of Ib or IIb was added to an 80% $CD_3CH_2OD{-}D_2O$ solution, which was approximately 0.35 *m* in sodium acetate and sodium deuterioxide, and the reaction followed by pmr, the final spectra were almost coincidental with each other and those of a similar reaction in the absence of acetate; the only difference was the appearance of the methyl resonance of the acetate ion, which overlaps that of the olefin IV. As in its reactions with sodium thiophenoxide and azide, this reaction of Ib showed the formation of considerable amounts of the

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[8] The product distribution for the first-order solvolysis of Ib in 80% aqueous ethanol as determined by pmr was: VI, 32; V, 41; and IV, 27 mole %. These values also differ somewhat from those previously reported.[3]

isomeric allenyl bromide IIb at approximately 50–75% completion; this material subsequently reacts without affecting the product distribution.

Kinetic Results. Using the titrimetric procedure of the previous study,[3] the activation parameters and the solvent deuterium isotope effect for the second-order reaction of Ib with sodium hydroxide in 80% aqueous ethanol have been measured. The kinetic results, summarized in Table III, lead to the values: $(k_{OD}/k_{OH})_{Ib} = 2.0 \pm 0.1$; $\Delta H^{\ddagger}_{Ib} = 26.0 \pm 0.7$ kcal/mole, and $\Delta S^{\ddagger}_{Ib} = 19.7 \pm 2.4$ eu at 298°K.[9]

Table III. Solvolysis of 3-Bromo-3-methyl-1-butyne (Ib) in Basic 80%[a] Aqueous Ethanol

Temp, °C	Solvent	[Ib]	[NaOH]	k_2^0, 10^{-3} l. mole^{-1} sec^{-1}
0.00	EtOH–H_2O	0.0344	0.0465	
0.00	EtOH–H_2O	0.0271	0.0465	0.191 ± 0.03^b
25.00	EtOH–H_2O	0.0385	0.0469	
25.00	EtOH–H_2O	0.0409	0.0469	$11.6 \pm 0.4^{c,d}$
25.00	EtOD–D_2O	0.0282	0.0380	
25.00	EtOD–D_2O	0.0296	0.0380	24.2 ± 0.4^c

[a] 0.552 mole % ethanol. [b] Calculated from the slope of the weighted least-squares line correlating ln $[(b - x)/(a - x)]$ *vs.* time to 50% reaction (see Experimental Section). [c] Extrapolated initial second-order rate constants from all the data from both experiments given in each case. [d] Value from ref 3 reproduced in this work within experimental error.

Kinetic data for the base-promoted solvolysis of the allenyl bromide IIb were obtained using the same techniques and similar conditions. These results are given in Table IV.

Table IV. Kinetic Results for Base-Promoted Solvolysis of 1-Bromo-3-methyl-1,2-butadiene (IIb) in 80% Aqueous Ethanol[a]

Temp, °C	Isotopic substitution	Added salt	*m*	k_2, 10^{-4} l. mole^{-1} sec$^{-1\,b}$
25.00	None	None		2.20
25.00	EtOD–D_2O	None		4.17
25.00	IIb-d_6	None		1.94^c
25.00	None	$NaNO_3$	0.20	2.14
25.00	None	NaCl	0.20	2.00
25.00	None	NaBr	0.20	1.82
45.02	None	None		42.6

[a] Concentration ranges: NaOH, 0.035–0.84 *M*; IIb, 0.30–0.037 *M*. Mole fraction ethanol, 0.5520. [b] Mean of the values for duplicate runs as calculated from the slopes of the weighted least-squares line fitting ln $[(b - x)/(a - x)]$ *vs.* time plots to 60% reaction (see Experimental Section); average deviation is ±1–2%; estimated accuracy ±3%. [c] Uncorrected for 15% isotopic impurity.

Since the samples of IIb always contained some of the more reactive propargyl bromide Ib (in concentrations just detectable by infrared or pmr), plots of the point-by-point integrated rate constants *vs.* fraction of reaction show pronounced initial curvature. However, rate coefficients evaluated from the slopes of the weighted least-squares line correlating plots of ln $[(b - x)/(a - x)]$ *vs.* time to *ca.* 60–65% reaction were reproducible within ±1–2% for different solvent and sample preparations with varying initial concentrations of base and substrate.[10]

Table IV, lines 4, 5, and 6, show that added sodium salts depress the rate of this reaction; at 0.2 *M* these fall in the following order of decreasing effectiveness: sodium bromide (−17%), sodium chloride (−9%), and sodium nitrate (−3%). The salt effects on the base-promoted solvolysis of Ib are much larger, but the relative effectiveness of the different salts is the same: sodium bromide (−38%), sodium chloride (−26%), and sodium nitrate (−17%).[3] The secondary kinetic deuterium effect in the reaction of methyl-deuterated IIb-d_6, $k_H/k_D = 1.15$ (corrected to 100% isotopic purity), is about half that observed for the reaction of Ib-d_6,[4] but the solvent-isotope effects are comparable, $(k_{OD}/k_{OH})_{IIb} = 1.90 \pm 0.04$. Activation parameters for the base-catalyzed solvolysis of IIb are: $\Delta H^{\ddagger}_{IIb} = 27.3 \pm 0.9$ kcal/mole and $\Delta S^{\ddagger}_{IIb} = 18.7 \pm 3.0$ eu at 298°K.[6]

The pmr studies described above were all carried out in deuterated basic media in order to determine approximate exchange rates for the acetylenic proton of Ib and the allenyl proton of IIb under the various conditions. With lyate ions present, the exchange of the acetylenic hydrogen of Ib was immeasurably fast in all cases. However, approximate rate constants for the exchange of the allenyl hydrogen of IIb could be obtained either from estimates of the rate of disappearance of the allenyl hydrogen absorption or from the time of collapse of the double allenyl methyl absorption to a singlet. As described in the Experimental Section, the concomitant rates of solvolysis of IIb were also estimated. With or without the addition of 1 equiv of sodium acetate, azide, and thiophenoxide, the exchange rates were 10–20 times faster than the over-all rate of reaction of IIb. In the absence of added base, thiophenoxide ion promoted the hydrogen exchange of Ib (Table II).

Discussion

The kinetic evidence for the course of the base-promoted reaction of the allenyl bromide IIb is entirely analogous to that presented earlier for the propargyl bromide Ib and establishes that the rate-determining step in this reaction also involves the loss of bromide ion from the conjugate base. The products produced in both the presence and absence of added nucleophiles show that the two reactions share a common intermediate, to which it is reasonable to assign the allene–carbene structure III.

The rate of its allenyl hydrogen exchange is 10–20 times faster than the rate of reaction of IIb to form other products. This is in accord with the preequilibrium proton loss, the first step of the mechanism of Figure 1, but not with a concerted α-elimination process. This situation is analogous to the base-promoted hydrolysis of $CHFCl_2$, for which the exchange rate was found to

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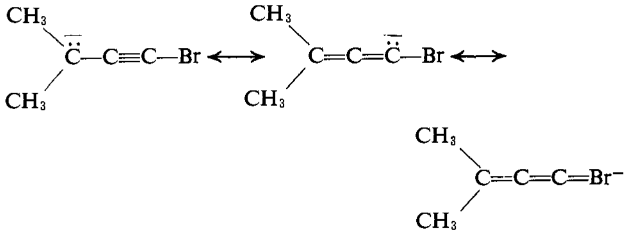
(9) (a) The parameters quoted are based on determinations at only two different temperatures and the *assumption* that the reaction obeys the Arrhenius equation. I. Fells and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 398 (1958), report that the alkaline hydrolysis of chloroform, which follows the same general mechanism, does not follow the Arrhenius equation over an extended temperature range. (b) The error limits were calculated from the expressions given by L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, 1, 8 (1963).

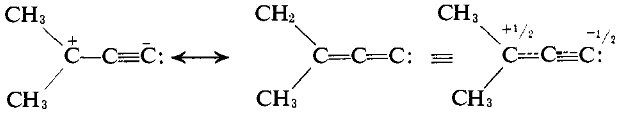
(10) Calculations show that rate constants for IIb determined by this method are not appreciably influenced by contamination of the sample with ~1 mole % of the more reactive isomeric Ib. This expectation is confirmed by the reproducibility of the results with many different samples of IIb which would be expected to vary in concentration of the trace impurity.

be 16 times the hydrolysis rate.[11] The exchange of IIb seems somewhat more facile than that of *cis*-1,2-dibromoethylene and much easier than that of ω-bromostyrene.[12] Therefore it seems reasonable to attribute some allylic resonance stabilization to the anion as well as some stabilization, owing to conjugative electron donation, to the bromine atom. The structure of the anion would thus be represented by the following resonance-contributing forms.



It appears quite likely, by analogy with the structures of ketenimines $(R_1R_2C{=}C{=}\ddot{N}{-}R)$, that the carbanion would be linear.[13]

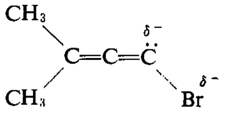
That the rate-determining step in the over-all process involves the loss of the bromide ion is demonstrated by the observation that the rate is depressed more by added sodium bromide than by the nonreactive noncommon ion salt, sodium nitrate. The depressive effect of added bromide is, moreover, only about half as large for the allenyl bromide as for the acetylene bromide. Such an effect is consistent with the suggestion of the earlier kinetic studies[3] that external return gives about one-half propargyl and one-half allenyl bromide; external return to form the much more reactive propargyl bromide would not be effective in slowing the solvolysis rate of the allenyl bromide. Thus the transition state in the over-all process occurs by heterolysis of the C–Br bond in the carbanion to produce the carbene III, whose electronic structure can be represented as follows.



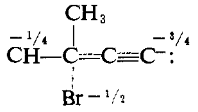
IIIa IIIb

In the MO picture on the right it is suggested that the carbene *spare pair* occupies the hybrid of the terminal carbon atom having considerable s character. The carbene *vacancy* would then exist in the highest of the two delocalized π orbitals formed by overlap of one p orbital on each of the three linear carbon atoms; if differences in overlap integrals, coulomb integrals, and bond distances are neglected, a crude first approximation of this π-electron distribution would be that of the allyl carbonium ion. This leads to the formal charges indicated.

In considering the structure of the transition state between the carbanion and carbene structures indicated above, an interesting problem arises. In the product (III), the orbital of the spare electron pair is oriented in the direction of bonding of the bromine in the carbanion. The change can therefore be thought of as a nucleophilic displacement of the bromide ion by the spare pair seeking the lower energy orbital with s character. This leads to the suggestion that the transition state may have a bent configuration because *two* p orbitals of the terminal carbon atom must be involved in forming two hybrids, one to bond with the bromine and the other to hold the spare pair.



The small depressive effect of the noncommon ion salt, sodium nitrate, indicates that the transition-state negative charge is only slightly more dispersed than that of the hydroxide ion of the initial state. This is consistent with the bent transition-state configuration, which reduces conjugation of the electron pair and negative charge dispersal into the π system. The noncommon ion salt effects on the base-promoted solvolysis of the propargyl bromide were much more negative, suggesting that the transition state in this process has a much more highly dispersed charge. This is expected for the generation of the allylic π system by departure of the negative bromide ion from the other end, which in the intermediate carries a partial positive charge. In this example a structure with the C–Br bond half-ionized would have a rough formal charge distribution as follows.



The secondary β-deuterium kinetic isotope effects in these and related solvolysis reactions are also consistent with the approximate relative charge distributions indicated above for the transition states and with the hypothesis that the β-deuterium effect on solvolysis reactions is, in closely related reactions, a relative probe for the degree of vacancy on the neighboring carbon atom.[4,14] Thus the effect observed with IIb-d_6 (k_H/k_{D_6} = 1.15) is only about one-half that for Ib-d_6 (k_H/k_{D_6} = 1.31), which is in turn only about half that for *t*-butyl-d_6 chloride (k_H/k_{D_6} = 1.71).[15] The solvent isotope effects are almost the same for Ib (k_{H_2O}/k_{D_2O} = 0.48) and IIb (0.50), consistent with their both reacting *via* formation of a carbanion intermediate. These values are characteristic of reactions in which proton attachment has neutralized the hydroxide ion and smaller than those which characterize nucleophilic displacement on carbon.[16] The other sources of the solvent isotope effect which should contribute in this mechanism are expected to be in opposing directions and apparently approximately cancel. The bromide ion formation[17] and carbanion hydrogen bonding (assuming behavior analogous to oxygen bases) would together contribute an effect of about 1.3 to 1.4 (k_{H_2O}/k_{D_2O}). This factor is not especially sensitive to reaction coordinate progress because more bromide ion

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[11] For a review of the mechanisms of basic haloform hydrolyses see J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, Chapter 3.

[12] S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

[13] J. J. Daly, *J. Chem. Soc.*, 2801 (1961).

[14] V. J. Shiner, Jr., H. R. Mahler, R. H. Baker, Jr., and R. R. Hiatt, *Ann. N. Y. Acad. Sci.*, **84**, 583 (1960).

[15] V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963).

[16] C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 3207 (1961).

[17] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, 37, 1491 (1959).

formation means less carbanion character and *vice versa*. This effect is approximately cancelled by the increase in CH initial-state frequencies on conversion to H_2O in the transition state. Since the acetylene CH frequencies are lowest, the gain is more in this example, giving a larger inverse contribution and a net larger inverse effect for the propargyl reactant, as observed.

The large positive $\Delta S^{\ddagger}$ values found for the reactions in this work are similar to those observed by Hine and co-workers[18] for the analogous E1cb reactions of the pentahaloethanes. Carbanion formations from pentahaloethanes in methanolic sodium methoxide[9] are characterized by small positive values for $\Delta S^{\ddagger}$, whereas some carbanion equilibria in aqueous solution[19] have strongly negative values for $\Delta S°$; thus there must be drastic enthalpy–entropy compensations in all of these reactions in polar media.[18]

The reactions of the intermediate III to give the various products are most interesting and instructive. The fact that the intermediate could be trapped with added thiophenoxide or azide is confirmatory evidence for its role in the mechanism. Although these trapping reactions were observed in the pmr tube and not carried out under closely controlled kinetic conditions, there is no doubt that they were dramatically accelerated by the extra added base. The products and yields were the same for the base-promoted reactions of the two halides, but in each case different from those obtained for the reactions which were not lyate ion promoted. This indicates that the two base-promoted processes share a common intermediate, to which we assign the structure III. The weak nucleophile, acetate ion, was not observed to react, indicating a relatively high electrophilic selectivity by III.

Comparison of reactions 3 and 5 of Table II, which have the same concentrations of bromide (Ib) and hydroxide but differing concentrations of thiophenoxide, indicates that thiophenoxide competes probably with lyate ions and not solvent molecules for the intermediate. Thus reaction 5, with relatively less thiophenoxide and more hydroxide, shows a larger yield of propargyl ether. (Since the olefin product in (5) was not observed, the phenyl thioether yields in this reaction are only relative and do not indicate the absolute drop.) If it is assumed that propargyl alcohol was produced in the same ratio to propargy ethyl ether in reactions 3 and 5 as indicated in Table I, the data of both these reactions indicate that the reactivity of thiophenoxide toward carbon is greater by a factor of ten than that of alkoxide plus hydroxide. That this ratio is the same for each reaction is consistent with the conclusion that propargyl ether is derived by reaction of the carbene with ethoxide although the limits of error are wide enough so that reaction with ethanol cannot be ruled out. Thus the general picture of nucleophilic attack on carbon of III is just the reverse of steps 3 and 4, Figure 1. Azide is estimated to be about five times as effective as alkoxide plus hydroxide, whereas bromide is only about one-tenth as effective and acetate was not observed to compete at all. This pattern of reactivity follows neither the order of the Swain–Scott nucleophilic constants[20] nor Pearson's[21] scale of relative "softness." It also remains to be explained why hydroxide and ethoxide prefer the propargyl to the allenyl position exclusively, while azide prefers it by a factor of eight, thiophenoxide by a factor of only about 1.6, and bromide attacks the two positions almost equally. In a hydrocarbon medium olefins attack predominantly at the allenyl position.[6]

The relative ease of attack by different anions at the two positions of the carbene can be correlated with the relative stabilities of the two possible intermediate ions, the acetylide and allenyl anions. Generally, because the sp orbital, which bears the negative charge in the acetylide, has greater electronegativity than the p orbital of the allene, the acetylide ion is expected to be the more stable.

Attack by hydroxide or alkoxide ions therefore gives the more stable acetylide ion and products derived from it. However, just as α-bromine atoms stabilize carbanions through d-orbital conjugation, bromide attack at the terminal allene position gives an allene carbanion with extra stabilization, and this process can compete more favorably with attack at the propargyl position. Thiophenoxide can also accept some back-bonding of the allenide negative charge to stabilize the carbanion produced by its attack on the terminal position; since this type of interaction is not operative to stabilize the negative charge produced at the remote position when nucleophilic attack occurs at the propargyl carbon, thiophenoxide attack at the allene position becomes competitive. The azide ion also has π orbitals to conjugate with the allenide negative charge, making attack by this ion at the allene position competitive. Thus, nucleophilic attack at the allene position of III seems to depend on some extra interaction to stabilize the negative charge in the transition state. An extreme manifestation of this is in the carbenoid addition to olefins where the extra negative charge which would result is stabilized by cyclopropane ring formation. The nonpolar hydrocarbon solvent used would be particularly conducive to allene attack by the neutral nucleophile because any charges produced would be in close proximity, whereas attack at the propargyl position would generate initially a zwitterion with relatively large charge separation. Thus, neutral nucleophiles, especially those which can donate a positive group or atom for simultaneous bonding, or perhaps ion pairs in nonpolar solvents, should be relatively more inclined to form allene products from III. That increased steric hindrance favors an increased proportion of allene derivative has been suggested[22] to explain the increased yield of allene quaternary ammonium salts from reaction of trimethylamine with more crowded tertiary propargyl halides. The rather large proportion (~28%) of allene derivative in the alkylation product from attack of sodium diethyl malonate on the zwitterion carbene[23] may also be due to the influence of steric effects. Two other more intriguing possibilities are: (a). a three-center attack involving simultaneous proton transfer to produce directly the more stable anion XIII, and (b). initial attack of the

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[18] J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *J. Am. Chem. Soc.*, **83**, 1219 (1961).

[19] R. G. Pearson, *ibid.*, **70**, 204 (1948).

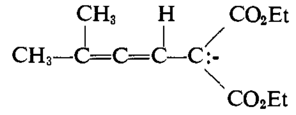
[20] C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

[21] R. G. Pearson, *ibid.*, **85**, 3533 (1963).

[22] G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, **30**, 3696 (1965).

[23] A. F. Bramwell, L. Crombie, and M. H. Knight, *Chem. Ind.* (London), 1265 (1965).

oxygen of the ambient nucleophile at the propargyl position followed by rearrangement.



XIII

The considerations which apply to a propargyl carbonium ion would be somewhat different. Here the direct product of nucleophilic attack by anions is not the carbanion but the acetylene or allene; the allene product would be slightly more stable and might predominate, but the shorter terminal bond would tend to make the positive charge of the ion concentrate at the propargyl position. Nucleophilic attack by low activation energy processes should, as observed,[8] give predominantly propargyl derivatives. That allene attack is possible is demonstrated by the well-known Meyer–Schuster rearrangement in which aqueous acid catalysis converts propargyl alcohols to α,β-unsaturated aldehydes or ketones, presumably *via* the allenyl alcohol.[24] Under these conditions, attack at the propargyl position would be expected to be reversible so the formation of the α,β-unsaturated carbonyl compound rather than the propargyl derivative is almost certainly the result of thermodynamic rather than kinetic control.

Direct Displacement Reactions. The results given in Table II seem to demonstrate clearly that in the *absence of strong base* the powerful thiophenoxide nucleophile can give a direct displacement reaction with both the propargyl and allenyl halides. Thus reaction 1 (Table II) shows relatively slow acetylenic hydrogen exchange and a product ratio quite different from the analogous base-promoted reaction 3. The substitution product from direct attack by thiophenoxide on Ib is exclusively the allenyl thiophenyl ether indicative of an $\mathrm{S_N2'}$ mechanism. Since nucleophilic addition of mercaptides to triple bonds has been characterized (at somewhat higher reaction temperature however), this $\mathrm{S_N2'}$ process is not unexpected.[25] Reaction 2 of the allenyl bromide also appears to be a direct displacement because of the absence of terminal proton exchange. The product proportions are not so different from those of the base-promoted process and indicate nearly equal facility of $\mathrm{S_N2}$ and $\mathrm{S_N2'}$ mechanisms for this reactant. The results of the reactions with azide ion alone are sufficiently complex so that it is impossible to determine the proportions of $\mathrm{S_N2}$ and $\mathrm{S_N2'}$ processes but both mechanisms seem to be involved in each case. Jacobs and Petty[26] have suggested that the propargyl bromide reacts with both lithium aluminum hydride and with sodium iodide in acetone by predominately $\mathrm{S_N2'}$ processes. The allene bromide gave somewhat less but still predominately the $\mathrm{S_N2'}$ reaction product with lithium aluminum hydride. These authors also obtained predominately the $\mathrm{S_N2'}$ product with thiophenoxide and the propargyl bromide but, in contrast to the present results reported, only $\mathrm{S_N2'}$ product from the reaction of thiophenoxide with the allene bromide.

Experimental Section

Proton magnetic resonance (pmr) spectra were obtained on a Varian A-60 spectrometer; δ values are given relative to internal tetramethylsilane. Infrared spectra were taken with Perkin-Elmer Infracord instruments.

3-Bromo-3-methyl-1-butyne (Ib) was prepared by a modification of two previous procedures.[3,27] A slight excess of phosphorus tribromide (270 g, 1 mole) was added with stirring to 252 g (3 moles) of 2-methyl-3-butyn-2-ol (V), the reaction mixture being kept at 5° under nitrogen. The volatile product was removed at low pressure and subsequently fractionally distilled through a Vigreux column. Relatively pure Ib was collected at 38–40° (100 mm); a more highly purified product was obtained after several high vacuum transfers of this material through a trap cooled to −63°; infrared absorption ($\mathrm{CCl_4}$) at 6490, 5900, 4410, 4340 (s), 4320, 4205, 4010 (w), 3300 ($\mathrm{C{\equiv}CH}$), 3100 (s), 2880 (s), 2955 (s), 2920 (s), 2100 (w), 1810 (m), and 1720 (m) cm^{-1}; and nmr peaks ($\mathrm{CCl_4}$) at δ 2.00 [6 H, singlet, $\mathrm{(CH_3)_2C{<}}$] and at δ 2.58 (1 H, singlet, $\mathrm{{\equiv}CH}$).

1-Bromo-3-methyl-1,2-butadiene (IIb) was prepared by the cuprous bromide catalyzed isomerization of Ib,[27,28] the progress of the reaction being followed by pmr. About 1 g of catalyst was added to 20 g of IIb in a small erlenmeyer flask containing a magnetic stirring bar. An apparent equilibrium mixture containing 95–96 mole % IIb and 4–5 mole % Ib was obtained after stirring for 36–48 hr at about 35°. IIb was never obtained without a trace of Ib, but about 10–15 g, greater than 97% pure by pmr, was obtained by 5–8 transfers in a high-vacuum line through a trap cooled to −45°; infrared absorption ($\mathrm{CCl_4}$) at 6000, 4410, 4350, 4290, 4205, 4050, 3075, 3000 (s), 2960 (s), 2920 (s), 2875 (s), 1960 (s, $\mathrm{C{=}C{=}C}$), 1550 broad (w), 1450 (s), 1365 (s), and 1350 (s) cm^{-1}; and pmr peaks ($\mathrm{CCl_4}$) at δ 1.83 (6 H, doublet, J = 2.5 cps, $\mathrm{(CH_3)_2C{=}C}$) and at δ 5.71 (1 H, septet, J = 2.5 cps, $\mathrm{{=}CHBr}$).

1-Bromo-3-methyl-*d*$_3$-1,2-butadiene-4,4,4-*d*$_3$ (IIb-*d*$_6$) was obtained by the above procedure from the deuterated precursors, V-*d*$_6$ (90% isotopic purity by pmr) and Ib-*d*$_6$[4] (89.5% isotopic purity by pmr): infrared absorption (neat): 3090, 2920 (CH stretch), 2250, 2200, 2060 (C–D stretch), 1960 (s) ($\mathrm{C{=}C{=}C}$), 1345, 1280, 1200, 1160 (vs), 1075, 1045 (s), 830, 775, and 700 (s), and pmr peaks ($\mathrm{CCl_4}$) at δ 5.76 (1 H, singlet, δ CHBr) and 1.78 (0.61 H, complex multiplet, $\mathrm{CHD_2}$ impurity).

Ethan-2,2,2-*d*$_3$-ol-*d* was prepared by exchange of malonic acid several times with $\mathrm{D_2O}$, separation by freeze-drying, and decarboxylation to acetic acid-*d*$_4$ by heating; the acetic acid-*d*$_4$ was reduced with lithium aluminum hydride in ether and hydrolyzed with $\mathrm{D_2O}$, and the product was isolated as the azeotrope by distillation.

3-Thiophenoxy-3-methyl-1-butyne (IX) and 1-Thiophenoxy-3-methyl-1,2-butadiene (X). Pmr studies of the reactions of Ib and IIb with sodium thiophenoxide in aqueous ethanol (Table II, reactions 1 and 2) indicated that the same S-alkylated products arise in both reactions but in different proportions. To 15 g of an 80% aqueous ethanol solution which was 3.45% sodium hydroxide (0.013 mole) and 9.49% thiophenol (0.013 mole), 0.597 g (0.00405 mole) of IIb was added. After the yellow solution had stood overnight several transfers in a high vacuum line from a trap at 0° into a trap at −24° yielded a colorless oil. The thioethers proved to be unstable at the temperatures of ordinary vacuum distillation. When Ib was treated with sodium thiophenoxide under the same conditions and purified by the same method, an oil which had a similar infrared spectrum to that from the reaction of IIb was obtained; pmr peaks ($\mathrm{CCl_4}$) at δ 1.48 [6 H, singlet, $\mathrm{(CH_3)_2C{<}}$] and δ 2.12 (1 H, singlet, $\mathrm{{\equiv}CH}$) for IX; δ 1.67 [6 H, doublet, J = 2.5 cps, $\mathrm{(CH_3)_2C{=}C{=}C}$] and at δ 5.65 (1 H, septet, J = 2.5 cps, $\mathrm{{=}CHBr}$) for X; at δ 7.00–7.64 (complex multiplet, aromatic H). In a larger scale reaction 20 mmoles each of Ib, sodium hydroxide, and sodium thiophenoxide in 16 g of 80% aqueous ethanol yielded 1.2 g (0.0076 mole, 36%) of a mixture of the isomeric thioethers which was two parts IX and one part X by pmr. Infrared evidence has earlier been reported to show that Ib reacts with sodium thiophenoxide in methanol to yield mainly the allenyl thioether X, whereas IIb reacts under similar conditions to yield a preponderance of the propargyl thioether IX.[26]

3-Azido-3-methyl-1-butyne (XI) and 1-Azido-3-methyl-1,2-butadiene (XII). The pmr spectrum of a reaction mixture 0.4 *m* in Ib and 0.4 *m* in sodium azide in 80% deuterium oxide–ethan-2,2,2-*d*$_3$-ol-*d* showed the following changes. After about 70 min, the intensity of the methyl resonance at δ 2.00 owing to Ib decreased about 30% with the concomitant appearance of two new methyl

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[24] G. F. Hennion, R. B. Davis, and D. E. Maloney, *J. Am. Chem. Soc.*, 71, 2813 (1949).

[25] W. E. Truce, H. G. Klein, and R. B. Kruse, *ibid.*, **83**, 4636 (1961).

[26] T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963); T. L. Jacobs and R. D. Wilcox, *J. Am. Chem. Soc.*, **86**, 2240 (1964).

[27] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

[28] G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

resonances of about equal heights at δ 1.48 and 1.66. After 10 hr, the Ib resonance was reduced about 80%, and about 20% of the total absorption visible in the methyl region was due to solvolysis products IV, V, and VI; only a small fraction of the initially formed azide products responsible for the resonances at δ 1.48 and 1.66 remained and two new broad methyl resonances had arisen at δ 1.58 and 2.08. The latter two peaks are attributed to two products arising by further reaction of the initial azide products. After 31 hr, the substrate was 95% consumed. The dominant final product was that giving rise to the δ 1.58 peak; some of the material responsible for the peaks at δ 1.66 and 2.08 as well as the solvolysis products remained. However, the material responsible for the δ 1.48 peak was completely absent. The metastable peaks at δ 1.48 and 1.66 are assigned to the simple substitution products XI and XII, respectively, the assigned order being the same as that found for other isomeric propargyl and allenyl derivatives. It was anticipated that the δ 1.66 peak would show the same doublet splitting observed for other allenyl derivatives if the reaction were carried out in a protonic medium. A reaction of Ib was therefore carried out in aqueous acetone-d_6 (0.45 mole fraction water) and it followed a similar course except that the dominant final product gave rise to a broad peak at δ 2.08. However, only a broadened *singlet* was observed to appear at δ 1.66 during the reaction. When Ib was allowed to react with hydrazoic acid in aqueous acetone an acetylenic hydrogen absorption appeared at δ 2.78 associated with the appearance of the methyl resonance of XI at δ 1.46. This assignment appears definite even if some other aspects of this reaction are uncertain.

Attempts to isolate either the initial or subsequently formed products of azide substitution were unsuccessful. Removal of the solvent under vacuum at low temperatures and extraction by carbon tetrachloride or ether gave an amorphous but reactive solid which could not be purified by crystallization or chromatography.

Products of Solvolysis Reactions of I and II. Aqueous ethanol reaction solvents were made up by weight even though the compositions are referred to in the traditional vol. % units; the mole fractions of water corresponding to 70, 80, and 90 vol. % aqueous ethanol are 0.582, 0.448, and 0.265, respectively.[29] The following procedure is typical of the experiments done to study the products of the first-order solvolysis. Ethan-2,2,2-d_3-ol (172.7 mg) containing 11.4 mole % water was added to a weighed nmr tube and 39.5 mg of water was added, giving a solution 42 mole % in water, or 82 vol. % ethanol, and the composition was confirmed by integration of the pmr spectrum. Ib, 23.7 mg (0.158 mmole), was added from a weight-calibrated 50-μl syringe to make a 0.75 *m* solution, and the reaction was followed by scanning the pmr spectrum.

The following description of the reaction of IIb in 80% aqueous ethanol illustrates the procedure used to study the products of the second-order reactions in basic aqueous ethanol solvent. To 172 mg of ethan-2,2,2-d_3-ol containing 11.4 mole % water, 48 mg of a 17.1% aqueous sodium hydroxide solution was added, giving a solution containing 0.175 mmole of base. As determined by integration of the pmr spectrum, the solvent contained 44 mole % water. Addition of 25.6 mg (0.174 mmole) of IIb gave a solution 0.82 *m* in base and substrate. The progress of the reaction was followed by scanning the pmr spectrum.

In the reaction of Ib the absorption of IIb produced by rearrangement somewhat obscures that of the enyne IV; these two products were visually estimated to contribute about equally. On further standing the IIb solvolyzed and there resulted no change in the relative yields of the final products. Since the methyl resonances of V and VI lie close together, the contribution of each to the total integral over both was estimated by the peak height ratio. The error of 3–4 mole % quoted in Table I was estimated from the reproducibility and the errors in measuring integrals and peak heights. That the propargyl products IV, V, and VI account quantitatively for the consumption of Ib or IIb was demonstrated by material balance calculated from integral heights in the following manner. A solution of the substrate in nonbasic solvent was prepared at the same molal concentration as that used in the basic solvolysis reaction. The integral value over the methyl absorption of the substrate relative to that of the isotopic methyl impurity of the ethan-2,2,2-d_3-ol was equal within the limits of error quoted above to that of the methyl absorptions of IV, V, and VI compared to the same standard.[30] Also, all peaks observed in the spectrum were identified as belonging to the products indicated.

In studies of the base-catalyzed reactions of Ib and IIb with sodium thiophenoxide or azide a more convenient but less accurate measurement was provided by comparison of the peak heights to that of a standard, the solvent isotopic impurity. As a check on the integral method for demonstrating the quantitative nature of the yield measurements, a certain weight of V was added to the solution after the reaction was complete. From the increase of peak height (or integral) and the weight of added alcohol, the scaling factor in millimoles per unit peak or integral height was computed. Assuming that this factor applied to all propargyl and allenyl methyl resonances and using the appropriate statistical factors, it was found that the amount of observed and identified products accounted to within 1 mg for all of the substrate introduced.

Pmr Studies of the Reactions of Ib and IIb with Sodium Thiophenoxide, Acetate, and Azide. The technique described above was used to follow the reactions of Ib and IIb with sodium azide, acetate, and thiophenoxide in the presence and absence of sodium hydroxide. The reaction mixtures were prepared by adding a deuterium oxide solution of the reagents of known composition to a weighed amount of ethan-2,2,2-d_3-ol-*d*; after this mixture was equilibrated in the probe and the spectrometer was adjusted to optimal conditions, the substrate was introduced from a microliter syringe calibrated to deliver the desired amount of material. The syringe could be calibrated to deliver a given weight of substrate with an accuracy of ±0.1 mg. After the addition, the tube was shaken vigorously, and the methyl region from δ 1.0 to 2.0 was rapidly and continuously scanned, the time of peak appearances being recorded with a stopwatch.

Kinetic Methods

A. Exchange Studies. A solution 0.25 *M* in IIb and 0.57 *M* in sodium deuterioxide in ethan-2,2,2-d_3-ol-*d* containing about 0.45 mole fraction deuterium oxide showed no pmr absorption characteristic of the allenyl hydrogen after about 3 min, and the doublet methyl absorption had collapsed to a singlet. The exchange was estimated to be at least 90% complete in about 2.5 min, which gives a minimum approximate nomographically estimated exchange rate constant, assuming second-order behavior, of 3×10^{-2} M^{-1} sec^{-1}.[31]

The amount of chemical reaction measured by the change in peak areas was similarly estimated to have a maximum value of 2×10^{-3} M^{-1} sec^{-1}. Thus the exchange rate exceeds the reaction rate by a factor of 15 or more. For the reactions in the presence of added nucleophiles the exchange process was followed by the rate of collapse of the doublet allenyl methyl resonance. These calculations involved an estimation of the molarity of the solutions from the molal concentrations used in the pmr studies. The rates of exchange in the presence of acetate, azide, or thiophenoxide were in the range of $1\text{–}5 \times 10^{-2}$ M^{-1} sec^{-1} and the reaction rate in all cases was 2×10^{-3} M^{-1} sec^{-1}.

B. Titrimetric Rate Studies. The base titration method of Shiner and Wilson[3] was used with some modifications to determine the rates of basic solvolysis of Ib and IIb. Aqueous ethanol and ethanol-*d*–deuterium oxide solvents were prepared by weight to contain 0.552 ± 0.001 mole fraction of alcohol.[29,32] Reagent grade sodium hydroxide was used to prepare carbonate-free 0.04–0.05 *M* basic aqueous ethanol sol-

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(29) B. L. Murr, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1961.

(30) Strictly speaking, integral comparisons of this type are valid only at low radiofrequency power or if the product of T_1 and T_2 is the same for the different types of hydrogens compared: 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, p 458. The latter restriction is probably fulfilled for the propargyl methyl resonances although extension to the allenyl methyl resonances may be a less satisfactory approximation.

(31) S. G. Smith and I. D. R. Stevens, *J. Chem. Educ.*, **38**, 574 (1961).

(32) W. E. Buddenbaum, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1964.

vent. A negligible amount of isotopic impurity is introduced by the hydroxide ion in the basic deuterated solvent used for measuring the solvent isotope effects. Normalities of the basic solvents were determined by adding 5-ml aliquots to 5 ml of standard 0.05 *M* hydrochloric acid in 50 ml of acetone and titrating to the lacmoid end point with standard aqueous, carbonate-free sodium hydroxide, appropriate blank corrections being made. The density of each basic solvent preparation was determined using a 25-ml Weld pycnometer. For kinetic runs in the presence of various added sodium salts, the dried reagent-grade salt was weighed into a 100-ml volumetric flask, basic aqueous ethanol was added, and the flask was reweighed. The volume of the solution was calculated from the density and total weight of basic salt-containing solvent.

For the kinetic experiments at 25°, the allenyl bromide was weighed into glass cups with easily removable ground caps which were dropped into the flasks at zero time. After vigorous shaking for 20–30 sec the flasks were returned to the bath. Ten to twelve aliquots per experiment were removed with solvent-calibrated, 5-ml pipets and quenched in 50 ml of cold acetone containing 5 ml of 0.05 *M* standard acid and lacmoid indicator; the excess acid was titrated with standard base delivered from a 5-ml microburet which could be read to ±0.01 ml. The titers usually ranged from 1 to 4 ml over *ca.* 60% reaction. The terminal reaction times were taken when the pipets were half-drained. The rate of the basic solvolysis of IIIb at 45° was determined using sealed tubes. Five-milliliter aliquots of a ~0.07 *M* basic solvent solution were added to Pyrex test tubes, constricted at the top and frozen in a Dry Ice–acetone bath. The same calibrated pipet was used to add aliquots of an approximately 0.06 *M* allenyl bromide solution to the frozen base solution. The frozen, sealed tubes were pre-equilibrated to 45° in a hot water bath for several minutes before placing them in the constant-temperature bath regulated to ±0.01°. Two frozen samples were retained for initial titers, and when the bath temperature became constant, two tubes were simultaneously withdrawn and quenched in a Dry Ice–acetone bath at time zero. Ten samples were taken and two tubes remained in the bath for 3 days for the infinity titrations. The frozen tubes were opened and quenched with 100 ml of acetone containing 10 ml of standard acid. A 10-ml microburet (±0.02 ml) was used to titrate the samples to the lacmoid end point. The rate at 25° was also determined by this method, and the value ($k_2 = 2.30 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$) was within 4.5% of that determined by the pipet technique.

For the kinetics of the base-catalyzed solvolysis of Ib, the substrate was weighed in a syringe and introduced into the flask, and the syringe was quickly reweighed before taking the first sample. The pycnometer and pipets were calibrated with solvent at 0° for the runs at that temperature. High initial values of $\bar{k}_2$ were more pronounced in these runs (*vide supra*) than in the 25° runs.

Treatment of Data. The kinetic data were analyzed by the use of the integrated second-order rate law in the form

$$\bar{k}_2 = \frac{2.303}{t(a - x)} \log \frac{b(a - x)}{a(b - x)}$$

where $\bar{k}_2$ is the integrated second-order rate constant, *a* and *b* are the initial concentrations of sodium hydroxide and organic bromide, respectively, and *x* is the concentration of material consumed at time *t* sec after the start of the reaction. The quantity *x* is evaluated from the following relationship

$$x = (N_{\text{NaOH}}V_{\text{NaOH}} - N_{\text{HCL}}V_{\text{HCL}})/(V_{\text{EtOH}} - N_{\text{EtOH}})$$

where N_{NaOH}, N_{HCl}, V_{NaOH}, and V_{HCl} refer to the normalities and volumes in milliliters of the standard sodium hydroxide and hydrochloric acid solutions. N_{EtOH} is the normality of the aqueous alcoholic base which made up the reaction mixture and V_{EtOH} is the aliquot volume in milliliters.

Except for the 0° experiments, initial integrated second-order rate coefficients, $\bar{k}_2^0$, for the solvolysis of Ib were evaluated by extrapolating plots of $\bar{k}_2$ *vs.* $100(x/a)$ to 0% reaction;[3] this was necessary because external return and isomerization caused the reaction to deviate from strictly second-order behavior.

Since all samples of IIb contained traces of the more reactive Ib the second-order rate coefficients for the initial points in these reactions were spuriously high; however, they did not fall off toward the end of the reaction because of isomerization. Therefore the second-order rate constants for these reactions were evaluated by a weighted least-squares treatment of the data for the plots of $\ln [(b - x)/(a - x)]$ *vs.* *t*. The second-order rate constants evaluated from the slopes of these lines were reproducible within ±2% for experiments involving different solvent and sample preparations as well as different initial concentrations and using different standard solutions. A description of the calculations, including the weighting method and the program used to calculate the results on an IBM 709 computer, is available in the thesis.[1a] Since the 0° reactions using Ib showed initially high values for the integrated second-order rate coefficients, $\bar{k}_2$, the weighted least-squares treatment was used to evaluate the second-order rate constants for these experiments.

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