The Kinetics of Bromination of 1,5-Dimethylnaphthalene. A Change in Mechanism[1]

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The kinetics of bromination of 1,5-dimethylnaphthalene in 90% aqueous acetic acid in the presence of bromide ion indicates that in this reaction the breaking of the carbon–hydrogen bond is part of the rate-controlling step. In contrast, in bromination of many other hydrocarbons under the same conditions, the first step alone controls the rate. The reversal of the mechanism is ascribed to steric crowding in the intermediate. Two bromo substitution products formed in the reaction have been synthesized and characterized. Addition of acetic acid accompanies substitution.

Aromatic bromination is known to proceed by the sequence

$$\mathrm{ArH} + \mathrm{Br_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArHBr^+} + \mathrm{Br^-}$$

$$\mathrm{ArHBr^+} \xrightarrow{k_2} \mathrm{ArBr} + \mathrm{H^+}$$

If the reaction is carried out in aqueous acetic acid and in the presence of an excess of bromide ion, the rate expression is

$$k_{\mathrm{obsd}} = kK/(K + \mathrm{Br^-}) \qquad (1)$$

where K is the dissociation constant of the tribromide ion,[4] and k_{obsd} is obtained from the experimental rate law, $-\mathrm{d}(\mathrm{Br_2})_t/\mathrm{d}t = k_{\mathrm{obsd}}(\mathrm{ArH})(\mathrm{Br_2})_t$.[4] This rate expression has been satisfied in the bromination of many different hydrocarbons and has been interpreted to mean that free bromine is the substituting entity and that the first step is rate-determining ($k_2 \gg k_{-1}$).[4,5] The absence of a significant primary isotope effect[6] and of acetate ion catalysis[4] confirms this view. The constant k refers to bromination by free, uncomplexed bromine and is obtained as the slope from a plot of k_{obsd} against $K/(K + \mathrm{Br^-})$. We now wish to report the results of a kinetic study of the bromination of 1,5-dimethylnaphthalene, where the kinetics reveal that the second step is partly rate controlling.

For a comparison with the reaction of 1,5-dimethylnaphthalene, the bromination of 2,3-dimethylnaphthalene was also studied. The bromination of this compound has the same kinetic characteristics as the reactions of all compounds previously studied. In Table I are listed rate constants for its bromination at varying bromide ion concentrations at a constant ionic strength ($\mathrm{NaClO_4}$) and in Figure 1 is shown the plot of k_{obsd} against $K/(K + \mathrm{Br^-})$. The slope, k, is 0.810 ± 0.015 l./mol sec. By contrast, for the bromination of 1,5-dimethylnaphthalene, the corresponding plot shows marked curvature for reaction in both 75 and 90% aqueous acetic acid (Table I, Figure 2). The deviation from a straight line is of such a nature as to suggest that expression 1 should have an additional bromide ion term in the denominator, *i.e.*

Table I

Kinetic Data for the Bromination of 2,3- and 1,5-Dimethylnaphthalene.[a] Dependence of Rate on Bromide Ion Concentration[b]

NaBr, mol/l.	2,3-Dimethylnaphthalene–90% acetic acid, $k_{\mathrm{obsd}} \times 10^2$	1,5-Dimethylnaphthalene–75% acetic acid, $k_{\mathrm{obsd}} \times 10^2$	1,5-Dimethylnaphthalene–90% acetic acid, $k_{\mathrm{obsd}} \times 10^3$
0.100	5.50	27.1	9.54
0.125	...	...	6.92
0.150	3.61	12.8	4.93
0.20	2.64	7.70	3.03
0.30	1.85	3.80	1.51
0.40	1.39	2.28	1.03
0.50	1.14	1.60	0.756

[a] All rate constants are in l. mol^{-1} sec^{-1}; T, 25°. [b] The total salt concentration was maintained at 0.50 M with $\mathrm{NaClO_4}$ where necessary.

$$k_{\mathrm{obsd}} = k'K/(K + \mathrm{Br^-})(\mathrm{Br^-}) \qquad (2)$$

Such a term should result from a mechanism in which a rapid equilibrium is established between reactants and the intermediate, followed by a rate-determining loss of the proton ($k_2 \ll k_{-1}$). A plot using expression 2 results in a straight line, but the points at lowest bromide ion concentrations fall below the line.

If the intermediate $\mathrm{ArHBr^+}$ is assumed to be present in a steady-state concentration, the observed rate constant is given by the complete expression

$$k_{\mathrm{obsd}} = \frac{k_1k_2K}{(k_{-1}[\mathrm{Br^-}] + k_2)(K + \mathrm{Br^-})} = \frac{k_1k_2K/k_{-1}}{(K + \mathrm{Br^-})[\mathrm{Br^-} + (k_2/k_{-1})]} \qquad (3)$$

In the bromination of 2,3-dimethylnaphthalene, as well as in previous brominations, $k_2 \gg k_{-1}[\mathrm{Br^-}]$ and expression 3 reduces to the observed expression 1. If $k_2 \ll k_{-1}[\mathrm{Br^-}]$, expression 2 results. Expression 3 will not completely reduce to 2 if the ratio k_2/k_{-1} is not negligible with regard to the bromide ion concentration. Equation 3 can be rewritten in the form $K/[(K + \mathrm{Br^-})(k_{\mathrm{obsd}})] = (k_{-1}[\mathrm{Br^-}]/k_1k_2) + (1/k_1)$. A plot of the left-hand side of the equation against $[\mathrm{Br^-}]$ results in a straight line, from which k_1 and the ratio k_{-1}/k_2 can be obtained (Figure 3). From such plots, k_1 is found to be 0.374 l./mol sec in 90% acetic

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[1] Kinetics of Aromatic Halogenation. XII.

[2] Taken in part from the Ph.D. Thesis of J. B. Kim, Bryn Mawr College; National Science Foundation Cooperative Fellow, 1965–1966; U.S. Steel Fellow in Chemistry, 1966–1967.

[3] Taken in part from the Senior Honors Thesis of M. Link, Bryn Mawr College, May 1964, and from a summer's work as a National Science Foundation Undergraduate Research Participant, 1963.

[4] E. Berliner and M. C. Beckett, *J. Amer. Chem. Soc.*, **79**, 1425 (1957).

[5] (a) L. Altschuler and E. Berliner, *ibid.*, **88**, 5837 (1966); (b) U. P. Zimmerman and E. Berliner, *ibid.*, **84**, 3953 (1962); E. Berliner and J. C. Powers, *ibid.*, **83**, 905 (1961).

[6] E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964); H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964). Substantial isotope effects have, however, been observed in the bromination of some crowded substrates. See P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960); E. Helgstrand, *ibid.*, **19**, 1583 (1965); E. Helgstrand and A. Nilsson, *ibid.*, **20**, 1463 (1966).

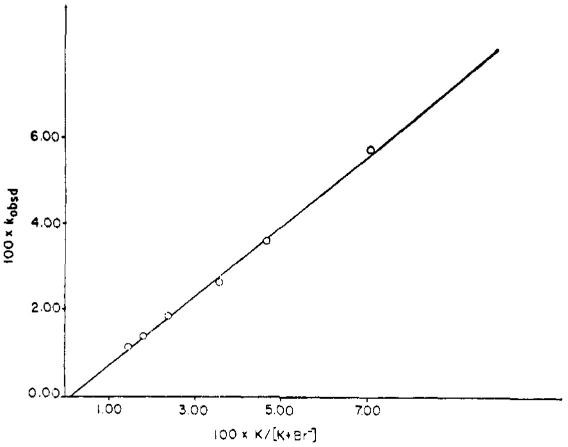

Figure 1.—The dependence of the rate of bromination of 2,3-dimethylnaphthalene on the bromide ion concentration: solvent, 90% acetic acid.

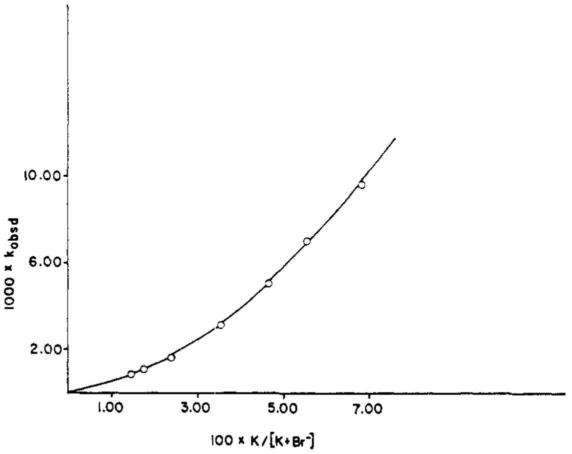

Figure 2.—The dependence of the rate of bromination of 1,5-dimethylnaphthalene on the bromide ion concentration: solvent, 90% acetic acid.

acid and 6.54 l./mol sec in 75% acetic acid and the ratios k_2/k_{-1} are 6.07×10^{-2} and 5.95×10^{-2}, respectively. The ratio k_2/k_{-1} can therefore not be neglected with regard to the bromide ion concentration, particularly when the latter is at its lowest value of 0.1 M. Bond breaking (k_2) becomes part of the rate-controlling step and the intermediate partitions itself between reactants and products in a measurable way. For every molecule of intermediate that goes onto the products, about eight return to reactants in both 90 and 75% acetic acid at a 0.5 M concentration of bromide ion. The constant k_1 is greatly affected by the polarity of the solvent but the ratio k_2/k_{-1} is not. The rate constant k_{-1} should be greater in the less polar solvent, because two ions react to form neutral molecules. Since the ratio k_2/k_{-1} stays the same, k_2 in the less polar solvent is probably also increased, which could happen if the hydrogen bromide in the products is not appreciably dissociated.

Support for the view that in the bromination of 1,5-dimethylnaphthalene the second step is partly rate determining comes from the observation of acetate ion catalysis. Such catalysis might be expected if carbon–hydrogen bond breaking were involved in the rate-determining step. The effect of acetate ion on the rate does not lend itself to a straightforward interpretation, because sodium acetate, like other salts, causes a positive primary salt effect. It has been observed in previous studies that the effect of acetate ion is less rate enhancing than the effect of sodium perchlorate.[4] This is shown for the bromination of 2,3-dimethylnaphthalene in Figure 4 and is typical of all of the other cases that have been investigated. However, in the bromination of 1,5-dimethylnaphthalene, the effect of acetate ion is considerably greater than that of perchlorate ion (Figure 4). Because this is the only compound for which this reversal of acetate *vs.* perchlorate has so far been observed, it is not unreasonable to assume that it reflects a genuine catalysis by acetate ions.[7]

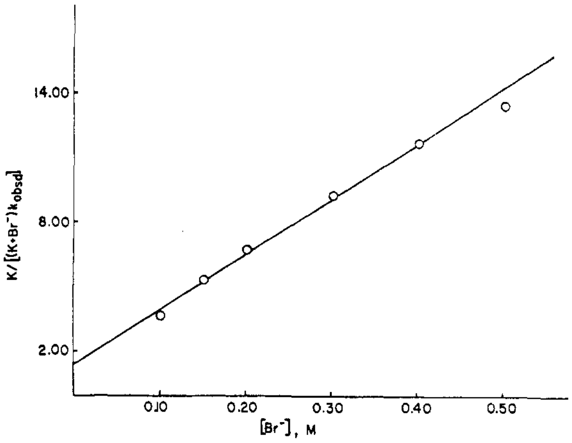

Figure 3.—The dependence of the rate of bromination of 1,5-dimethylnaphthalene on the bromide ion concentration: solvent, 75% acetic acid; slope, 2.57 mol sec l.$^{-1}$; intercept, 0.153 mol sec l.$^{-1}$.

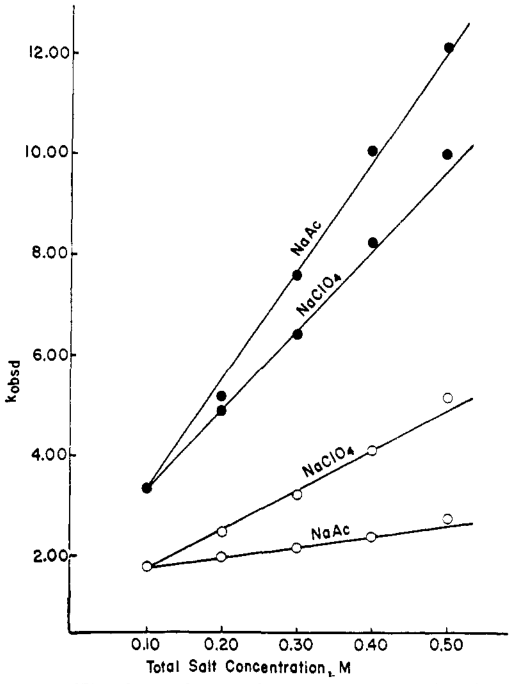

Figure 4.—The dependence of the rate of bromination on the salt concentration: upper graph, 1000 × k_{obsd} for 1,5-dimethylnaphthalene; lower graph, 100 × k_{obsd} for 2,3-dimethylnaphthalene; solvent, 90% acetic acid; [NaBr], 0.10 M in all runs.

The results of the bromination of 1,5-dimethylnaphthalene are very reminiscent of Zollinger's

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(7) Kinetic characteristics very similar to those observed in the bromination of 1,5-dimethylnaphthalene have now also been found in the bromination of 1,4-dimethylnaphthalene: K. Judd, unpublished results.

studies on the diazo coupling of G-salt[8] and a similar interpretation probably holds. The intermediate in the bromination of the 4 position of 1,5-dimethylnaphthalene is sterically crowded because of the methyl group in the 5 (*peri*) position, just as it is in the diazo coupling of G-salt by the 8-sulfonate group. Steric crowding favors return of the intermediate by loss of bromine to the less hindered reactants, rather than reaction by loss of a proton to the more hindered product. In other words, the condition $k_{-1}[\mathrm{Br}^-] \gg k_2$ is the result of the steric requirements of the intermediate. This does not seem to manifest itself in a large decrease of k_1, because k_1 is within a factor of 2 of the value calculated from the additivity principle. Instead, it results in an increase in k_{-1}, in a decrease in k_2 and hence in an over-all decrease of k_2/k_{-1}.

No bromo substitution products of 1,5-dimethylnaphthalene have been described in the literature and authentic samples of two were prepared and identified as follows. In order to avoid the formation of acetoxy addition products (see below), preparative bromination was carried out in chloroform or carbon disulfide in the dark. The product consisted of three monobromo compounds. Separation of the two major isomers was facilitated, because 2-bromo-1,5-dimethylnaphthalene does not form a stable picrate. Other naphthalene derivatives with a methyl group and a bromine atom *ortho* to each other were also found to form unstable picrates, which cannot be recrystallized. Consequently, the reaction mixture from a bromination in carbon disulfide, which contained more of the 4 isomer, was treated with an excess of picric acid. A pure picrate was easily obtained and from it a monobromo compound of mp 41.8–42.6°. This was converted *via* the lithium compound and dimethyl sulfate into the known 1,4,5-trimethylnaphthalene; hence the compound of mp 41.8–42.6° is 4-bromo-1,5-dimethylnaphthalene. The second compound was obtained by crystallization of the crude reaction mixture. This compound of mp 78.0–78.3° was converted into the known 1,5-dimethyl-2-naphthoic acid and its methyl ester and is therefore 2-bromo-1,5-dimethylnaphthalene. The third isomer, which was obtained only in small amounts, was not isolated or characterized but is presumably the 3-bromo compound. The nmr spectrum of 4-bromo-1,5-dimethylnaphthalene confirmed the assigned structure. The assignment was based on the known observation that a bromine atom will shift the *meta* protons to higher fields. The spectrum of 1-bromo-4-methylnaphthalene, for instance, shows a doublet at 394.5 Hz downfield from TMS with a splitting of 7.5 Hz and each component of the doublet is split into a quartet by the 1-methyl group (coupling ~1 Hz). Analogously, the spectrum of 4-bromo-1,5-dimethylnaphthalene contains a doublet at 398 Hz with a splitting of about 8 Hz. The upfield absorptions are absent in the spectrum of 4-bromo-1,2-dimethylnaphthalene and of 1,5-dimethylnaphthalene, which do not possess a proton *meta* to bromine. A complete analysis of the spectrum of the hydrocarbon has since been made.[9]

The reaction mixture of the kinetic runs in 90% acetic acid consisted of 72.6% of 4-bromo-1,5-dimethylnaphthalene, 19.2% of 2-bromo-1,5-dimethylnaphthalene, and 7.7% of the unidentified 3-bromo isomer. These bromo compounds constitute about 60% of the total products. The remaining 40% consists of three other compounds, which are acetoxy compounds, formed from addition of acetic acid to the intermediate and subsequent aromatization during vpc analysis. The acetoxy products were not identified, but their presence was inferred from the typical infrared absorption bands in the reaction mixture prior to vpc analysis. Their formation is analogous to the formation of acetoxy compounds in the bromination of phenanthrene and anthracene.[5a,10] In the present case, loss of a proton has presumably the highest activation energy of the reactions available to the intermediate and addition to the intermediate competes effectively with proton loss. Because of the reaction of the intermediate with acetic acid, the constant k_2, as obtained from Figure 3 (k_{-1}/k_2), is really composite and represents the disappearance of the intermediate not only by loss of a proton but also by reaction with acetic acid. The occurrence of addition during substitution is in itself the result of steric crowding in the intermediate, which is responsible for the increase in k_{-1} and the decrease in k_2. In the bromination of no other of the dimethylnaphthalenes have acetoxy products been observed,[7] but one is also formed in the bromination with bromine and silver perchlorate of the hindered 1,3,5-tri-*t*-butylbenzene.[11]

From k_1 and the isomer distribution and from data obtained previously,[5a] it is possible to calculate partial rate factors ($f_2 = 2.65 \times 10^7, f_3 = 1.06 \times 10^7, f_4 = 1.00 \times 10^8$), but these do not accurately reflect the reactivities in the three positions. Some of the products are very likely formed by decomposition of acetoxy or dibromo addition compounds. The unusual change of isomer distribution with change in solvent (36.6% of the 2-bromo compound is formed in chloroform, but only 18.8% in carbon disulfide) is possibly the result of such secondary reactions, as is the unexpectedly large amount of 3-bromo isomer. Assuming that the additivity principle holds, and with the help of earlier data, one can calculate that at least 98% of substitution should take place in the 4 position and less than 2% in the 2 position. The large difference between predicted and observed values is probably only partly due to decomposition of addition compounds; it is partly the result of steric hindrance in the intermediate, which reflects itself in less substitution in the 4 position, and consequently more in the 2 position. In the only direct substitution reaction previously reported, namely, the chloromethylation of 1,5-dimethylnaphthalene, only the formation of the 2 isomer has been recorded.[12]

A kinetic expression similar to eq 2, but not 3, would be obtained if the rate-controlling step were to involve an attack by a bromine cation. In view of the difficulty of obtaining bromine cations from

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[8] H. Zollinger, *Helv. Chim. Acta.*, **38**, 1597, 1617, 1623 (1955).

[9] J. B. Kim and J. M. Anderson, *Spectrochim. Acta.* in press.

[10] For similar addition during chlorination, see P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961); P. B. D. de la Mare and R. Koenigsberger, *ibid.*, 5327 (1964); and others in the series.

[11] P. C. Myhre and G. S. Owen, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1965, 48 S.

[12] W. Ried and H. Bodem, *Ber.*, **91**, 1354 (1958).

bromine molecules,[13] this latter interpretation can be ruled out.

The participation of carbon–hydrogen bond breaking in the rate-determining transition state, as observed here, is usually detected through an isotope effect, but the kinetics of bromination have characteristics such that it can be inferred without the use of isotopically labeled compounds.

Experimental Section

Materials.—All inorganic reagents were best reagent grade chemicals which were dried at 110° before use. The glacial acetic acid was purified with chromium trioxide as described before.[4,5] Percentages of aqueous acetic acid are by volume, before mixing. 2,3-Dimethylnaphthalene was recrystallized three times from an ethanol–benzene (about 6:1) mixture and melted at 104.5–104.9°[14] (lit.[15] mp 104–104.5°). The 1,5-dimethylnaphthalene was recrystallized from ethanol; it melted at 81.2–81.8° (lit.[16] mp 82°).

Separation of the pure bromo compounds was facilitated when, after several attempts at isolation, seed crystals became available and when it was observed that the 2-bromo isomer does not form a stable picrate. It was also found that solutions of picrates could be injected into the vpc injection port without prior isolation of the hydrocarbon; the picric acid remained on the column.

2-Bromo-1,5-dimethylnaphthalene.—To 15 g (0.0975 mol) of 1,5-dimethylnaphthalene in 45 ml of carbon disulfide was added with stirring 6 ml of Br_2 (0.117 mol) in 30 ml of CS_2. Stirring was continued over night, excess Br_2 was destroyed with $NaHSO_3$, and the product was washed with water and dried. Material boiling between 121 and 136° (5 mm) was allowed to solidify in the cold and several crystallizations from ethanol–water afforded 1.13 g (4.93%) of material melting at 77.3–78.5°. A sample, recrystallized further, melted at 78.0–78.3°. *Anal.*[17] Calcd for $C_{12}H_{11}Br$: C, 61.29; H, 4.72. Found: C, 61.12; H, 4.80.

To 200 mg (0.00085 mol) of the above compound, dissolved in 5.0 ml of anhydrous ether, was added 1 ml of *n*-butyllithium in hexane (approximately 0.0034 mol). After 15 min of vigorous stirring, the solution was poured on a Dry Ice–ether slush. After work-up and crystallization from ligroin with 2 drops of glacial acetic acid, there was obtained 75 mg (44%) of 1,5-dimethyl-2-naphthoic acid of mp 207–208° (lit.[18] mp 205–207°). The methyl ester, recrystallized from methanol, had mp 75.9–76.4° (lit.[18] mp 77–78°).

1-Bromo-4,8-dimethylnaphthalene.—A run similar to the one above was conducted in CS_2. A large forerun from the distillation consisted of 95% of unreacted hydrocarbon. The main fraction (8.00 g, 30.6%) consisted of over 70% of the 4 isomer. Preparation and two recrystallizations of the picrate of the distillate afforded a product which was 99% pure on vpc. A total of 2.00 g of picrate was obtained, which, when decomposed on an alumina column, afforded 0.90 g (3.68%) of a white crystalline solid, mp 40.9–42.3°. A sample recrystallized further from ethanol had mp 41.8–42.6°. *Anal.* Calcd for $C_{12}H_{11}Br$: C, 61.29; H, 4.72. Found: C, 61.17; H, 4.72. The picrate, prepared from the pure solid, melted at 122.1–123.6°. It could not be obtained analytically pure, in spite of numerous crystallizations with or without excess of picric acid. It probably contained some free bromo compound. *Anal.* Calcd for $C_{18}H_{14}O_7N_3Br$: C, 46.57; H, 3.04. Found: C, 49.61; H, 3.50. The above bromo compound (300 mg, 0.0013 mole) was converted into the lithium derivative as described for the other isomer. The light yellow solution was treated with a solution of 0.11 ml (0.0015 mole) of dimethyl sulfate in 5 ml of anhydrous ether. The solution became white and turbid. After 15 min of stirring, the mixture was gently refluxed for 1 hr. After work-up, the product was dissolved in the smallest amount of hot ethanol and 0.20 g of picric acid was added. After two recrystallizations from ethanol, a picrate of mp 145.7–147.5° was obtained (lit.[19] mp 144–145°), which was 96.1% pure. The picrate, after decomposition with dilute ammonia, afforded white plates of 1,4,5-trimethylnaphthalene, which after recrystallization from ethanol–water melted at 61.9–62.8° (lit.[19] mp 63°). The literature melting points of the other two possible trimethylnaphthalenes are below 60°.[19,20]

Bromination of 1,5-dimethylnaphthalene in carbon disulfide affords, in the order of their retention times, 9.4% of the 3 isomer, 18.8% of 2 isomer, and 71.8% of 4 isomer, while in chloroform the proportions, in the same order, are 11.3, 36.6, and 52.1%.

Kinetic Determinations.—These determinations were carried out as described in previous work.[4,5] The temperature was 25° for all runs. Rate constants were obtained graphically from the integrated form of the second-order rate equation by the method of least squares. The initial bromine concentration was determined from the intercept of the graphs but the value never differed appreciably from that taken from the initial titer. For very fast reactions the initial titer was determined from a blank. Several blank determinations, which were identical with the kinetic runs except that the hydrocarbon was omitted, showed that loss of bromine was negligible and did not have to be taken into account. The concentration of bromine varied between 0.001 and 0.004 *M* and that of the hydrocarbons between 0.004 and 0.01 *M*, depending on the rate of the individual reactions. All runs were done at least in duplicate and the average values listed in Table I rarely had an average deviation of more than 2%. Rate constants were not affected by a change in reactant concentration. For instance, at a concentration of sodium bromide of 0.10 *M* and of sodium perchlorate of 0.40 *M*, rate constants of 9.38 and 9.49 × 10^{-3} were obtained for the bromination of 1,5-dimethylnaphthalene in 90% acetic acid when the concentrations of bromine were 0.00115 and 0.00231 *M* and those of hydrocarbons 0.00401 and 0.00803 *M*, respectively.

The equilibrium constant *K* was taken as 0.0110 mol/l. in 75% and 0.0073 mol/l. in 90% acetic acid.[21]

Product Analyses.—The conditions of typical kinetic runs were reproduced for the product analysis. The reaction mixtures were 0.0040 *M* in 1,5-dimethylnaphthalene, 0.10 *M* in NaBr, 0.40 *M* in $NaClO_4$, and approximately 0.001 *M* in Br_2; the total volume was usually 100 ml. The completed runs were extracted with five 20-ml portions of petroleum ether and also with three 20-ml portions of benzene. The petroleum ether extracted over 90% of the hydrocarbons and bromo derivatives, but benzene was necessary to extract also the acetoxy compounds. Six products were formed, in addition to excess unreacted hydrocarbon. Comparison with chromatograms of the products of bromination of the hydrocarbon according to their retention times established that the first three were monobromination products. The first was assumed to be the 3-bromo compound and the second and third were identified as the 2- and 4-bromo derivatives, respectively. From three independent kinetic runs, and six chromatographic determinations, the amounts of bromo compounds were established as 7.7 ± 2.3%, 19.2 ± 1.2%, and 72.6 ± 2.7%. Because of the similarity in structure of the bromo compounds, peak areas were taken to represent also weight ratios; the same was done for the acetoxy compounds. The acetoxy peaks overlapped and their relative areas could not be determined with great accuracy. Their percentages, determined from two kinetic runs and four chromatographic determinations, were 23.0% ± 3.0%, 48.3 ± 12.3%, and 28.7 ± 12.4%. The bromination products constituted 59.2 ± 4.2% (two runs, four chromatograms) and the acetoxy compounds 40.7 ± 4.1% of the total. The benzene extract of a run conducted on four times the scale listed above showed, prior to vpc analysis, the typical infrared acetoxy absorptions at 1230 and 1755 cm^{-1}. The same absorption bands were shown by an authentic sample of 2-naphthyl acetate. In kinetic runs extracted only with petroleum ether, the weaker absorption at 1230 cm^{-1} was absent. The acetoxy compounds obtained on vpc analysis

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[13] E. Berliner, *J. Chem. Educ.*, **43**, 124 (1966).

[14] All melting points are corrected.

[15] G. Schroeter, L. Lichtenstadt, and D. Irineu, *Ber.*, **51**, 1587 (1918).

[16] O. Kruber and A. Marx, *ibid.*, **72**, 1970 (1939).

[17] All analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

[18] D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2090 (1956).

[19] L. Ruzicka and L. Ehmann, *Helv. Chim. Acta.*, **15**, 140 (1932).

[20] J. Harvey, I. M. Heilbron, and E. D. Kamm, *J. Chem. Soc.*, 3136 (1926); I. M. Heilbron and D. G. Wilkinson, *ibid.*, 2537 (1930).

[21] A. E. Bradfield, G. I. Davies, and E. Long, *J. Chem. Soc.*, 1389 (1949); T. W. Nagakawa, L. J. Andrews, and R. M. Keefer, *J. Phys. Chem.*, **61**, 1007 (1957).

were not characterized further, but, to verify that aromatic acetoxy compounds have longer retention times than bromo compounds, a test mixture was run consisting of 1-methylnaphthalene, 1-bromo-4-methylnaphthalene, and 1-acetoxy-4-methylnaphthalene. The difference in retention time between the bromo and acetoxy derivatives of 1-methylnaphthalene is very similar to that of the derivatives of 1,5-dimethylnaphthalene. Furthermore, when the response factors of the monomethyl compounds were used to calculate weight per cent of a kinetic run, the weight of bromo to acetoxy compounds was found to be 56.9 to 43.1%, in good agreement with the ratio given above.

In the bromination of 2,3-dimethylnaphthalene, a 97.4% yield of 1-bromo-2,3-dimethylnaphthalene was obtained. It was characterized by a comparison with the retention time of an authentic sample, which was prepared according to a literature procedure and had mp 61.8-62.8° (lit.[22] mp 63-64°). The 2.6% constitute another monobromo isomer, most likely the 5 isomer (1-bromo-6,7-dimethylnaphthalene). Material balances on three runs were 97.9, 68.8, and 93.5%. Chromatography of the total reaction product on an SE-30 column showed that no acetoxy products were present. No dibromo substitution products were detected in the bromination of either hydrocarbon.

The gas chromatographic analyses were done on a programmed temperature gas chromatograph (F & M Scientific Corp., Model 720). For the separation of the bromo isomers a 4 ft × 0.25 in. column of 5% Apiezon L-5% Bentone 34 on 80-100 Diatoport S was used. Hydrocarbons were analyzed on a 2 ft × 0.25 in. column of Carbowax 20M on 80-100 Diatoport S and acetoxy compounds on a 6 ft × 0.25 in. column of 5% SE-30.

The infrared spectra were recorded in chloroform on a Perkin-Elmer Infracord, Model 137, and the nmr spectra on a Varian Model A-56/60-A spectrometer.

Registry No.—1,5-Dimethylnaphthalene, 571-61-9; 2-bromo-1,5-dimethylnaphthalene, 15095-53-1; 4-bromo-1,5-dimethylnaphthalene, 15095-54-2; 4-bromo-1,5-dimethylnaphthalene picrate, 15153-26-1.

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[22] R. T. Arnold and R. W. Liggett, *J. Amer. Chem. Soc.*, **64**, 2875 (1942).

Reactions of Conjugated Nitro Olefins with Phosphoranes and with Dimethylsulfoxonium Methylide to Give Ylides and Nitrocyclopropanes, Respectively[1a]

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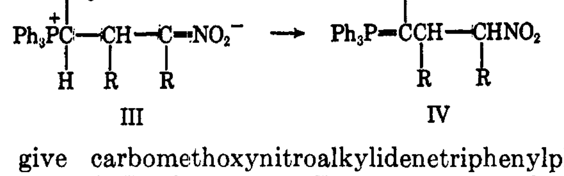
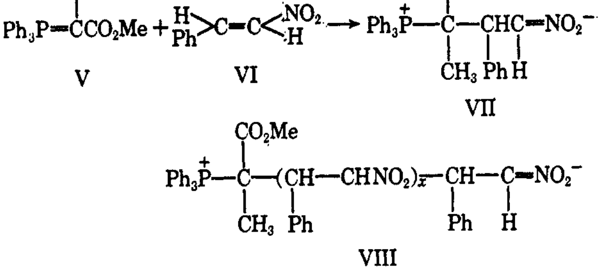
Carbomethoxymethylenetriphenylphosphorane (I) and conjugated nitro olefins (II) react with subsequent proton transfer to give phosphorus ylides, carbomethoxynitroalkylidenetriphenylphosphoranes (IV). The structures of IV were established from their infrared and ultraviolet absorptions. Chemical evidence for the structure of a typical phosphorane (X) was obtained by its bromination and subsequent regeneration by aqueous sodium carbonate. Methylenetriphenylphosphorane (XIV) and dimethylsulfoxonium methylide (XVIII) react with conjugated nitro olefins to yield nitrocyclopropanes; XVIII is the much more efficient and convenient reagent. The spectral properties of various nitrocyclopropanes are described.

Carbomethoxymethylenetriphenylphosphorane (I)[2] has been presently found to add to various conjugated nitro olefins (II, Table I) at 90° in hydrocarbon solvents with subsequent proton transfer (eq 1)



$$\underset{\text{I}}{Ph_3P{=}CHCO_2Me} + \underset{\text{II}}{{}^{R}_{H}{>}C{=}C{<}^{NO_2}_{R}} \longrightarrow \underset{\text{III}}{Ph_3\overset{+}{P}\underset{H}{\overset{CO_2Me}{C}}{-}\underset{R}{CH}{-}\underset{R}{C}{=}NO_2^-} \longrightarrow \underset{\text{IV}}{Ph_3P{=}\overset{CO_2Me}{C}\underset{R}{CH}{-}\underset{R}{CH}NO_2} \quad (1)$$

to give carbomethoxynitroalkylidenetriphenylphosphoranes (IV) efficiently.[3] Reaction of I and II or thermolysis of IV resulting in expulsion of triphenylphosphine to give nitrocyclopropanes, isoxazoline oxides, or related products could not be effected advantageously. Carbomethoxyethylidenetriphenylphosphorane (V)[2] reacts with β-nitrostyrene (VI) to give multiple adducts (VIII, eq 2). Phosphonium nitronates (VII) which do not self-neutralize to nitroalkylphosphoranes (IV) thus may continue Michael addition to conjugated nitro olefins.[3]



$$\underset{\text{V}}{Ph_3P{=}\overset{CH_3}{C}CO_2Me} + \underset{\text{VI}}{{}^{H}_{Ph}{>}C{=}C{<}^{NO_2}_{H}} \longrightarrow \underset{\text{VII}}{Ph_3\overset{+}{P}{-}\underset{CH_3}{\overset{CO_2Me}{C}}{-}\underset{Ph}{CH}\underset{H}{C}{=}NO_2^-} \xrightarrow{\text{VI}}$$

$$\underset{\text{VIII}}{Ph_3\overset{+}{P}{-}\underset{CH_3}{\overset{CO_2Me}{C}}{-}(\underset{Ph}{CH}{-}CHNO_2)_x{-}\underset{Ph}{CH}{-}\underset{H}{C}{=}NO_2^-} \quad (2)$$

The phosphorus ylides (IV) prepared by the new method are stable greenish white solids which can be recrystallized conveniently from hydrocarbons and from ethyl acetate. The structures of the products as phosphoranes (IV) are assigned from their infrared absorptions (Table I) for nitro (6.48-6.51 μ)[4] and phosphoranocarbonyl (6.13-6.23 μ) groups and from

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[1] (a) This research was supported by the Office of Naval Research. (b) To whom inquiries should be addressed.

[2] (a) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953); (b) O. Isler, H. Guttman, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1956).

[3] H. J. Bestmann and F. Seng [*Angew. Chem.*, **74**, 154 (1962)] have reported a similar reaction in that I reacts with methyl benzoylacrylate to give triphenylphosphine and [(1-carbomethoxy-2-benzoyl)ethyl]carbomethoxymethylene.

[4] J. F. Brown Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1955).