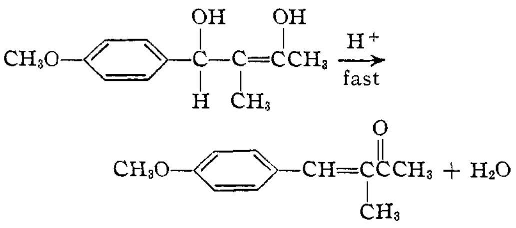 (12)

paper[15] indicates that under certain circumstances, enolization does in fact represent an important reaction path for the dehydration of β-hydroxyketones.

Temperature Coefficients.—The temperature coefficients for the various reaction processes discussed above have been measured. The data are presented in Table V.

As expected, the entropy of activation for the condensation step, k_1^0 (calculated to H_0 of zero), is far smaller than that of the various other steps because of the larger molecularity of this particular reaction relative to the others. The addition of another neutral molecule to an activated complex usually subtracts about 15 entropy units of translational entropy from the entropy of activation in aqueous solution[16]; the same phenomenon in organic solvents is attended by a decrease in the entropy of activation of about 25–28 entropy units. It is seen that the entropy of activation for the condensation step, k_1^0, is reasonable.

TABLE V

TEMPERATURE COEFFICIENTS FOR REACTION STEPS

Reaction conditions	T, °C.	$k_1^0 \times 10^5$ l. mole^{-1} sec.$^{-1}$	$k_2 \times 10^5$ sec.$^{-1}$	$k_3 \times 10^5$ sec.$^{-1}$
VII in anhyd. acetic acid; 0.2 M sulfuric acid	25.15			See Table I
	35.39			24.8
	35.39			24.9
	45.51			71.1
	45.51			72.9
	54.28			170
$\Delta H^{\pm}$				20.2 kcal.
$\Delta S^{\pm}$				−11 e.u.
VII in acetic acid, 0.400 M sulfuric acid; 0.96% water	25.15	14.2	7.75	11.22
	35.39	28.1	22.6	37.3
	45.51	52.2	65.4	116.4
$\Delta H^{\pm}$		11.5	19.5 kcal.	21.4 kcal.
$\Delta S^{\pm}$			−39 e.u.	− 8 e.u.
VII in 33.5% sulfuric acid	25.15		4.90	3.18
	35.39		16.3	9.88
	45.51		52.2	31.4
$\Delta H^{\pm}$			21.6 kcal.	21.0 kcal.
$\Delta S^{\pm}$			− 7 e.u.	− 9 e.u.

The correlations of a variety of reactions with the acidity function H_0 in acetic acid solutions serve to support the utility of this function in such a solvent. However, it must not be concluded that questions of detailed mechanism may be decided from such results in non-aqueous solvents. We must regard the conclusions drawn here as tentative.

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[15] D. S. Noyce and W. Reed, THIS JOURNAL, to be published.

[16] R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Solvent Effects in the Reactions of N-Bromosuccinimide with Toluene, Fluorene and Acenaphthene; Evidence for a Polar Mechanism in Propylene Carbonate

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RECEIVED MARCH 18, 1958

In carbon tetrachloride or benzene, N-bromosuccinimide reacts with toluene, fluorene and acenaphthene to introduce a bromine atom on a methyl group or methylene group adjacent to an aromatic ring. In propylene carbonate, a highly polar solvent, nuclear substituted products are obtained with all three hydrocarbons. When a molar equivalent of boron trifluoride is added, the reaction of fluorene with N-bromosuccinimide in benzene also gives largely the nuclear substituted product, but small amounts of 9-bromofluorene also are formed.

The generally accepted mechanism for the Wohl-Ziegler reaction,[1] in which N-bromosuccinimide is used to introduce a bromine at a carbon atom adjacent to a double bond or an aromatic ring, involves a free radical chain reaction. This mechanism, suggested by Bloomfield,[2] is supported by several facts: (1) The reaction is catalyzed by benzoyl peroxide,[3] azobisisobutyronitrile[4] and cumene hydroperoxide.[4] (2) The reaction is inhibited by hydroquinone, dinitrobenzene, bromanil and iodine.[5] (3) The effects of *m*- and *p*-substituents on the side-chain bromination of toluene[6] are in accord with this mechanism. (4) The observed stereospecificity in brominations of bibenzyl and acenaphthene with N-bromosuccinimide[7] constitutes proof of a two-step mechanism for side-chain bromination and is powerful evidence in support of the Bloomfield suggestion.

Other reactions of N-bromosuccinimide, however, suggest that this reagent may also react by an ionic mechanism involving a heterolytic dissociation of the N–Br bond. Significant among these are the many reported nuclear brominations of aromatic

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[1] (a) A. Wohl, *Ber.*, **52**, 51 (1919); (b) K. Ziegler, A. Spaeth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942). For more recent review articles see: (c) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); (d) T. D. Waugh, "N-Bromosuccinimide, Its Reactions and Uses," Arapahoe Chemicals, Inc., Boulder, Colo., May, 1951.

[2] G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

[3] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

[4] H. J. Dauben, Jr., and E. A. Youngmann, unpublished results. These and additional results by H. J. Dauben, Jr., and L. L. McCoy (*vide infra*) are discussed by C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 382.

[5] H. J. Dauben, Jr., and L. L. McCoy, unpublished results.

[6] E. C. Kooyman, R. Van Helden and A. F. Bickel, *Konikl. Ned. Akad. Wetenschap. Proc.*, **56B**, 75 (1953).

[7] F. D. Greene, W. A. Remers and J. W. Wilson, THIS JOURNAL, **79**, 1416 (1957).

hydrocarbons and aryl ethers[1c,d,8] and instances in which N-bromosuccinimide reacts by addition to a double bond as well as by allylic substitution.[9] The nuclear brominations are catalyzed by Lewis acids such as the chlorides of aluminum, zinc and iron,[10] and the bromine addition reactions are strongly promoted by the addition of inorganic salts and alkylammonium salts.[9d,f] Both of these observations are indicative of an ionic mechanism.

It has been suggested that the course of the Wohl–Ziegler reaction may be markedly dependent upon the choice of solvent, and the regular use of carbon tetrachloride may be an essential factor in contributing to the success of the α-methylenic substitution.[11] This suggestion is *a priori* reasonable, since a more polar or more ionizing solvent might favor a heterolytic rather than a homolytic dissociation of the N–Br bond. However, when N-bromosuccinimide reacts in water or alcohols, hydrolysis or alcoholysis converts the reagent to either hypobromous acid or an alkyl hypobromite, and it is these latter reagents, rather than N-bromosuccinimide itself, which effect the actual brominations.

It occurred to us that the use of propylene carbonate as the reaction medium might suitably test the hypothesis that N-bromosuccinimide is capable of directly effecting an ionic bromination in a polar solvent. This solvent is highly polar; its dielectric constant is 64.6 at 25°.[12] More important, propylene carbonate has no functional grouping which might be expected to be subject to facile attack by N-bromosuccinimide and, in fact, a solution of N-bromosuccinimide in this solvent still gives a positive starch–iodide test after 72 hours at room temperature or three hours at 100°, although at the higher temperature some bromine coloration is generated.

In accord with the foregoing, the present paper reports a study of the reactions of N-bromosuccinimide with toluene, fluorene and acenaphthene, all in propylene carbonate. In carbon tetrachloride, with benzoyl peroxide as catalyst, toluene reacts with N-bromosuccinimide in a rapid reaction to yield 64% of benzyl bromide.[3] In the presence of metal halides the reaction is much slower and gives 21–71% of *p*-bromotoluene.[10] The results of a study of the reactions of toluene with both N-bromosuccinimide and bromine in propylene carbonate are summarized in Table I. The reactions of Table I are accompanied by some attack on the solvent, propylene carbonate. This results in the formation of varying amounts of the two bromohydrins, 1-bromopropanol-2 and 2-bromopropanol-1, as described in the Experimental section. In the absence of added initiator or inhibitor, the reaction of N-bromosuccinimide with toluene in propylene carbonate resulted in three products, *o*-bromotoluene, *p*-bromotoluene and benzyl bromide. When benzoyl peroxide, an initiator, is added to the reaction, the amount of nuclear bromination is decreased, and the side-chain bromination is promoted. Conversely, the addition of an inhibitor, chloranil, had the opposite effect. The side chain bromination was suppressed, and the nuclear bromination was favored.

Table I

Bromination of Toluene in Propylene Carbonate

Reagent	Added substance	Yield, % Benzyl bromide	 *p*-Bromotoluene	 *o*-Bromotoluene
NBS	None	29.9	24.6	12.3
NBS	Benzoyl peroxide	72.5	3.3	1.9
NBS	Chloranil	14.0	36.5	18.5
Br_2	None	0	40.7	22.7

These results strongly support the hypothesis that in propylene carbonate N-bromosuccinimide reacts with toluene by both a radical chain mechanism and an ionic mechanism. If only a radical chain mechanism were involved the addition of either catalyst or inhibitor would alter the rate of reaction but not the product composition. Since in this solvent we obtain both the side-chain bromination product, which we normally associate with a free radical mechanism, and nuclear bromination products, which normally result from ionic reactions, and since we can suppress or promote the formation of either type of product by adding either an inhibitor or initiator for the radical chain reaction, it is clear that at least two mechanisms are operating simultaneously and competitively in this system.

It might be argued that the nuclear bromination products result from the adventitious presence of hydrogen bromide, which reacts with N-bromosuccinimide to form bromine, which then brominates the aromatic ring. The hydrogen bromide formed in this latter reaction can then react with more N-bromosuccinimide to generate more bromine. In actual fact bromine reacts readily with toluene in propylene carbonate to give the products indicated in Table I. This alternative explanation cannot be excluded on the basis of the experiments discussed thus far. However, the results with fluorene make this possibility highly improbable.

Fluorene reacts with N-bromosuccinimide in either carbon tetrachloride or benzene to give good yields of 9-bromofluorene,[13] and we have obtained an 84% yield of 9-bromofluorene from the reaction in benzene. However, when the reaction is run in benzene in the presence of one equivalent of boron trifluoride etherate, the product, again obtained in good yield, is largely 2-bromofluorene, and only small amounts of 9-bromofluorene are formed. This is contrary to Schmid's report[10] that boron trifluoride is ineffective in catalyzing the nuclear bromination. The structure of the 2-bromide was confirmed by its oxidation to 2-bromofluorenone.

In propylene carbonate N-bromosuccinimide reacts rapidly with fluorene to give 2-bromofluorene, and in this case no 9-bromofluorene is formed. The

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(9) (a) D. R. Howton, This Journal, **69**, 2060 (1947); (b) E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1519 (1947); (c) P. Couvreur and A. Bruylants, *Bull. soc. chim. Belg.*, **61**, 253 (1952); (d) E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952); (e) E. J. Corey, This Journal, **75**, 2251 (1953); (f) W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525, 689 (1955).

(10) H. Schmid, *Helv. Chim. Acta*, **29**, 1144 (1946).

(11) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1948, p. 256.

(12) R. P. Seward and E. C. Vieira, *J. Phys. Chem.*, **62**, 127 (1958).

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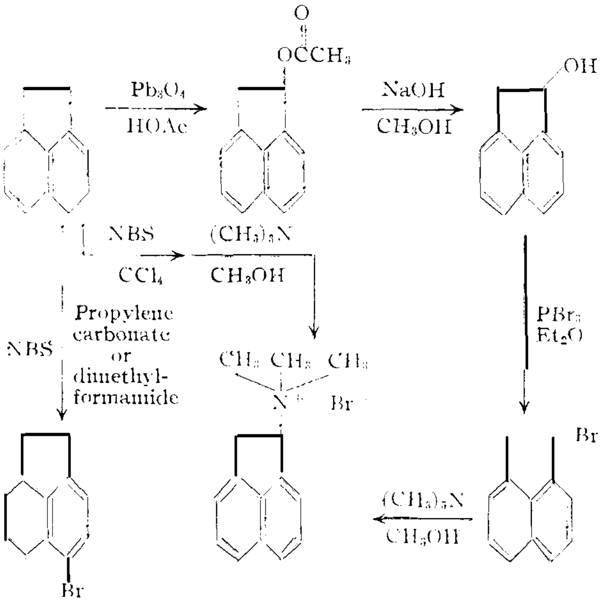
same nuclear substituted product is obtained when fluorene is treated with bromine in this solvent. However, when run under identical conditions, the reaction with N-bromosuccinimide is at least twenty-five times faster than the reaction with bromine. This gross difference in reaction rate makes it certain that N-bromosuccinimide is not just an intermediary source of molecular bromine in these ionic brominations and constitutes convincing evidence for the hypothesis that N-bromosuccinimide is capable of reacting *via* two paths, one involving ions and one involving a free radical chain.

It has been reported by some workers that the reaction of acenaphthene and N-bromosuccinimide in carbon tetrachloride results in the nuclear bromination product, 5-bromoacenaphthene,[8] and by others that reaction takes place on the side-chain to give 1-bromoacenaphthene.[7,14] We have studied this reaction in a way which avoided the isolation of the relatively unstable 1-bromoacenaphthene. This was done by converting the bromide, without prior isolation, to a quaternary ammonium salt with methanolic trimethylamine. An authentic sample of the known 1-acenaphthenyl-trimethylammonium bromide was obtained by preparing 1-acenaphthenol,[15] converting it to the bromide with phosphorus tribromide[16] and quaternizing with trimethylamine.[17] With equimolar quantities of acenaphthene and N-bromosuccinimide a 62% yield of quaternary ammonium salt was obtained, and this yield can be increased to 75% by using an excess of the hydrocarbon. These results, summarized below, show that, in carbon tetrachloride, the attack is on a methylene group and not on an aromatic ring. In both propylene carbonate and dimethylformamide, another polar solvent, the reaction with N-bromosuccinimide proceeds by a different path to give the nuclear substituted product, 5-bromoacenaphthene. This ability of N-bromosuccinimide to react by two mechanisms and to give either nuclear or side-chain bromination products, depending on the solvent used, adds to the great usefulness of this reagent. In many instances, the use of N-bromosuccinimide in propylene carbonate to effect nuclear brominations may be more convenient than the use of molecular bromine.



Experimental

Reactions of N-Bromosuccinimide with Toluene.—In a typical experiment N-bromosuccinimide (18.8 g., 0.105 mole) was added to toluene (36.8 g., 0.40 mole) in propylene carbonate (200 cc.), and the mixture was warmed in a water-bath until the solution did not give a starch–iodide test. The solution turns orange-red, then yellow. A second portion of N-bromosuccinimide (18.8 g., 0.105 mole) was added, and the heating was continued until the N-bromosuccinimide was consumed. The total reaction time was less than two hours. The reaction mixture was distilled at 20 mm. until the head temperature attained the boiling point of propylene carbonate (115° (20 mm.)). The distillate was then redistilled at 18 mm. and separated arbitrarily into three fractions. The three fractions were analyzed with a Perkin–Elmer 154B vapor fractometer using an A column at 140° and 18 pounds helium pressure. The positions of the peaks were checked with the known compounds, and synthetic mixtures were prepared and analyzed until one which duplicated the unknown was obtained. Propylene carbonate and benzyl bromide were not separated by the column, since they had the same retention time. These two compounds appeared together only in the third fraction, and this fraction was analyzed for benzyl bromide by hydrolysis and then a Volhard titration. Thus it was shown that this total product contained 0.052 mole of *p*-bromotoluene, 0.026 mole of *o*-bromotoluene, 0.063 mole of benzyl bromide and 0.006 mole of the mixed propylene bromohydrins.

When the reaction was run as above but with the addition, initially, of 0.6 g. of benzoyl peroxide, the products obtained were 0.153 mole of benzyl bromide, 0.007 mole of *p*-bromotoluene, 0.004 mole of *o*-bromotoluene, 0.011 mole of 1-bromopropanol-2 and 0.001 mole of 2-bromopropanol-1.

When 0.1 g. of chloranil was added initially, the products were 0.073 mole of *p*-bromotoluene, 0.037 mole of *o*-bromotoluene, 0.028 mole of benzyl bromide, 0.017 mole of 1-bromopropanol-2 and 0.001 mole of 2-bromopropanol-1.

In the reaction with bromine, the procedure was identical except that the N-bromosuccinimide was replaced with bromine (32 g., 0.20 mole). The products in this case were 0.0813 mole of *p*-bromotoluene, 0.0454 mole of *o*-bromotoluene, 0.1402 mole of 1-bromopropanol-2 and 0.0176 mole of 2-bromopropanol-1.

Reactions with Fluorene. (a) **In Benzene.**—To fluorene (50 g., 0.30 mole) in dry benzene (250 ml.) was added N-bromosuccinimide (56 g., 0.31 mole), and the mixture was refluxed 4 hours. After cooling the succinimide formed was filtered, and the benzene was removed *in vacuo*. The crystal mass was taken up in hexane (250 ml.), and the solution was decolorized with charcoal and filtered. On cooling a first crop of 51 g. of 9-bromofluorene was obtained. Concentration of the mother liquors gave a second crop of 12.5 g. of white needles. The yield was 84%, m.p. 102–104°.

(b) **In Benzene with Boron Trifluoride Etherate.**—To a solution of fluorene (16.6 g., 0.1 mole) in benzene (100 ml.) in a three-necked flask, fitted with a mechanical stirrer and reflux condenser was added redistilled boron trifluoride etherate (14.2 g., 0.1 mole). N-Bromosuccinimide (17 g., 0.095 mole) then was added slowly with stirring. The reaction mixture was refluxed 15 minutes, after which time the solution did not give a starch–iodide test. After cooling, the solid which precipitated was filtered and digested with hexane. The hexane solution was added to the benzene, and the combined solutions were evaporated *in vacuo*. The residue was taken up in hexane, and the solution was decanted from some tar that was present. Concentration of the hexane solution again yielded small amounts of tar. The solution was once more decanted from the tar, and concentration of this solution yielded finally 21 g. (90%) of the crude product, m.p. 78–82°. By fractional crystallization of this product from hexane and ethanol it was possible to

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(15) L. F. Fieser and J. Cason, THIS JOURNAL, **62**, 432 (1940).

(16) W. E. Bachmann and J. C. Sheehan, *ibid.*, **63**, 204 (1941).

(17) G. Wittig and H. Ludwig, *Ann.*, **589**, 55 (1954).

isolate only a single pure compound, 2-bromofluorene, m.p. 110–111°.

In another experiment portions of the crude product were treated as described below. The crude product (8 g.) was refluxed with trimethylamine (30 ml. of a 25% solution in methanol) in acetone (100 ml.) for one hour. The solvent was removed *in vacuo*, and the residue was taken up in ether. The ether solution was extracted two times with water, and the combined water extracts were extracted again with ether. Removal of the water gave a crude product which was crystallized from isopropyl alcohol to yield 0.86 g. of the known fluorenyl-trimethylammonium bromide,[18] m.p. 185–190° dec. The combined ether extracts yielded 6.8 g. of the crude 2-bromofluorene, m.p. 83–87°.

The crude product (5 g.) in a solution of sodium dichromate (25 g.) in acetic acid (30 ml.) and water (10 ml.) was refluxed 0.5 hour. More acetic acid (60 ml.) was added, and the solution was refluxed 2.5 additional hours. The reaction mixture was poured into water. The solid which precipitated was filtered and taken up in benzene. The benzene solution was dried and the solvent was removed *in vacuo* to yield 4.6 g. of crude product, m.p. 125–138°. Crystallization from alcohol gave 3 g. of 2-bromofluorenone, m.p. 141–146°. The oxidation of purified 2-bromofluorene (2 g.) gave 1.73 g. (82%) of the ketone, m.p. 146–148°.

(c) **In Propylene Carbonate.**—A mixture of N-bromosuccinimide (17.8 g., 0.1 mole) and fluorene (16.6 g., 0.1 mole) in distilled propylene carbonate (125 ml.) was warmed in a 60° bath for 2 minutes. The solution became warm and turned orange, and the solid dissolved. After 30 minutes at room temperature the color turned to yellow, and no starch–iodide test was obtained. The solution then was poured into 2 liters of water. The precipitate was filtered, sucked partly dry and taken up in benzene. The benzene solution was decanted from the water, dried and concentrated to yield 23.2 g. (97%) of white solid, m.p. 87–94°. Fractional crystallization from ethanol indicated the product was almost exclusively 2-bromofluorene, m.p. 110–111°; a mixed melting point with the product from the reaction in the presence of boron trifluoride etherate showed no depression.

When the crude product (8 g.) was treated with trimethylamine, as in the preceding experiment, the aqueous extracts contained no product, and the crude bromide (m.p. 90–96°) was recovered quantitatively from the ether extracts.

Oxidation of the crude product (5 g.) as before gave 4.5 g. of crude ketone, m.p. 130–143°. Crystallization of this product resulted in 3.5 g. of 2-bromofluorenone, m.p. 142–144°, and an additional crystallization from ethanol raised the melting point to 146–148°.

Reaction of Fluorene with Bromine in Propylene Carbonate.—To fluorene (16.6 g., 0.1 mole) in propylene carbonate (100 ml.) was added, with stirring, bromine (15 g., 0.094 mole) in propylene carbonate (50 ml.). The reaction mixture was kept at 70° for 2.5 hours, at which time the solution gave a negative starch–iodide test. The solution was poured into water, the solid was filtered and taken up in benzene, and the benzene solution was dried over Drierite. Removal of the solvent gave 22.5 g. of crude product, m.p. 72–80°. Crystallization from a minimum quantity of ethanol gave 17.0 g. (in two crops) of crude 2-bromofluorene, m.p. 99–103°

In another experiment the total crude product was subjected to fractional crystallization from ethanol. The product proved to be almost entirely 2-bromofluorene, although, in this case, it was possible to separate trace amounts (0.2 g.) of 2,7-dibromofluorene, m.p. 160–163°. This suggests that the crude product must have contained some unreacted fluorene, but this was not isolated.

Qualitative Relative Rates of Reaction of Fluorene with N-Bromosuccinimide and with Bromine in Propylene Carbonate.—To fluorene (16.6 g., 0.1 mole) in 150 ml. of propylene carbonate in a two-necked flask fitted with a mechanical stirrer and kept at constant temperature in a water-bath at 70° was added N-bromosuccinimide (16 g., 0.09 mole). After 5 minutes this solution did not give a starch–iodide test. To fluorene (16.6 g., 0.1 mole) in 100 ml. of propylene carbonate in a two-necked flask at 70° was added bromine (15 g., 0.094 mole) in propylene carbonate (50 ml.). The solution was added dropwise over a 5-minute period. Starch–iodide tests were made on the stirred solution at regular intervals. After 2 hours the solution still gave a positive starch–iodide test.

Reactions with Acenaphthene. (a) **In Carbon Tetrachloride.**—A suspension of N-bromosuccinimide (8.9 g., 0.05 mole) and acenaphthene (7.7 g., 0.05 mole) in carbon tetrachloride (100 ml.) was heated in a water-bath at 85°. The vigorous reaction was complete after 10 minutes. The solution was cooled to room temperature, and the succinimide was filtered. Removal of the solvent *in vacuo* left an orange oil which would not crystallize. The oil was taken up in acetone and treated with trimethylamine (25 ml. of a 25% solution in methanol). Removal of solvent gave a solid which was dissolved in a mixture of ether and water. The ether layer was separated, and the water layer was washed several times with ether. Concentration of the water solution *in vacuo* gave a yellow-white solid which was crystallized from isopropyl alcohol; yield 9 g. (62%), m.p. 206–207° dec. after recrystallization from isopropyl alcohol. This product showed no depression on mix-melting with an authentic sample of 1-acenaphthenyl-trimethylammonium bromide, prepared by the method of Wittig and Ludwig.[17]

By using an excess of acenaphthene (0.065 mole of the hydrocarbon to 0.025 mole of N-bromosuccinimide) in a small amount of carbon tetrachloride (30 ml.), the yield of the quaternary ammonium salt was increased to 75%. In this case the ether extracts were dried and concentrated, and 7 g. of crude crystals was obtained. Crystallization from ethanol gave 4.6 g. of acenaphthene, m.p. 96–98°. A yellow color persisted in the mother liquors, but no compound other than acenaphthene could be isolated.

(b) **In Dimethylformamide.**—A solution of N-bromosuccinimide (18 g., 0.1 mole) in dimethylformamide (50 ml.) was added to a suspension of acenaphthene (15.4 g., 0.1 mole) in dimethylformamide (50 ml.) at room temperature. Heat was evolved, and after 2 hours, the solution was poured into 1.5 liters of cold water. Filtration gave 23 g. (98%) of crude product. Crystallization from ethanol gave 18.5 g. (79%) of 5-bromoacenaphthene, m.p. 51–52°. A mixed melting point with an authentic sample of 5-bromoacenaphthene, prepared by bromination of acenaphthene, showed no depression.

(c) **In Propylene Carbonate.**—N-Bromosuccinimide (18 g., 0.1 mole) was mixed with acenaphthene (15.4 g., 0.1 mole) and suspended in distilled propylene carbonate (100 ml.). Heat was evolved immediately, and after 10 minutes the pale-yellow solution did not give a starch–iodide test. The solution was poured into water (2 liters); the crystals were filtered, sucked partly dry and taken up in benzene. The benzene solution was decanted from the water and dried over magnesium sulfate. The benzene was blown off with air, and the solid obtained was dried overnight *in vacuo*; yield 22 g. (94.4%), m.p. 48–52°. Crystallization from ethanol gave 19.2 g. of white platelets, m.p. 53–54°. Recrystallization gave 15.5 g., m.p. 53.5–54.5°, no depression on mix-melting with an authentic sample of 5-bromoacenaphthene.

North Adams, Mass.

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