In a similar way di-*p*-phenoxyphenyl ketone was made from duryl *p*-phenoxyphenyl ketone and phenyl ether. A mixture of 1.0 g. of the duryl ketone, 20 ml. of phenyl ether and 20 ml. of polyphosphoric acid was brought to 150° over a 1-hr. period and maintained at that temperature for 6 hr. The yield of di-*p*-phenoxyphenyl ketone was 41%.

URBANA, ILL.

[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions of Polymers with Reagents Carrying Two Interacting Groups. II. Bromine Displacement from α-Bromoacetamide and the Bromoacetate Ion by Poly-(methacrylic Acid) and Poly-(vinylpyridine Betaine)[1,2]

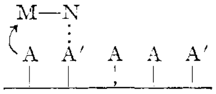
BY HARRY LADENHEIM AND HERBERT MORAWETZ

RECEIVED MARCH 16, 1959

The second-order rate constants for bromine displacement from α-bromoacetamide by carboxylate groups of singly and doubly ionized dicarboxylic acids show a very slight increase of reactivity with increasing basicity of the carboxylate. The carboxylates in partially ionized poly-(methacrylic acid) are 4–10 times as reactive as those in the dicarboxylic acids and their reactivity decreases sharply with rising degree of ionization of the polymer. A similar effect was observed with poly-(vinylpyridine betaine) which displaces bromine from both bromoacetamide and bromoacetate, although the reaction rate of its monofunctional analog 4-methylpyridine betaine is not experimentally observable. All these observations may be accounted for by a concentration of the low molecular weight reagent in the region of the macromolecular coil. The dependence of the reaction rate of poly-(methacrylic acid) with bromoacetamide on the degree of ionization of the polymer suggests that the amide is bound to the carboxyl groups and that the bond is stronger when the carboxyls are un-ionized.

Introduction

In a previous report[3] we described the result of the first of a series of studies concerned with the reaction rates of polymers with bifunctional reagents. The main purpose of this program is to define conditions leading to coöperative effects as represented below diagrammatically. Here the functional group A carried by the polymer is engaged in a displacement reaction on M, while the energetic interaction between A′ and N serves to accelerate the reaction by stabilizing the transition state. The groups A and A′ may be identical or may represent different states of ionization of the groups attached to the polymer chain.[4]



(1)

In the present investigation we measured the rates of bromine displacement from α-bromoacetamide and bromoacetate ion by partially ionized poly-(methacrylic acid) and by isoelectric poly-(4-vinylpyridine betaine), which were compared with the analogous reaction of singly or doubly ionized dicarboxylic acids and 4-methylpyridine betaine.

Experimental

Materials.—Bromoacetic acid and α-bromoacetamide were obtained as in the previous investigation.[3] Glutaric acid was recrystallized from benzene (m.p. 96.5°, neutralization equivalent weight 66.8). Maleic anhydride recrystallized from chloroform (m.p. 52°, neutralization equivalent weight 49.7) was used to prepare solutions of maleic acid. Fumaric acid (m.p. 282°) had a neutralization equivalent weight 58.7.

The preparation of 4-methylpyridine betaine which has not been reported previously was carried out as described for pyridine betaine.[5] The product lost one mole of water of crystallization when heated at atmospheric pressure at 100° and decomposed at 180°. The ultraviolet spectrum had maxima at 232 mμ (ε 6710) and 257 mμ (ε 4630).

Anal. Calcd. for $C_8H_9NO_2 \cdot H_2O$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.64; H, 6.72; N, 8.38.

Poly-(methacrylic acid) was prepared from methacrylic acid diluted with a sixfold volume of methanol and containing 1.6×10^{-3} mole of azo-bis-isobutyronitrile initiator per mole of monomer by heating for 20 hours at 65°. The polymer solution was diluted with water, exhaustively dialyzed and freeze-dried. The drying of the polymer was completed under reduced pressure at 50°. The carboxyl content determined by potentiometric titration was in exact agreement with theory; the light scattering molecular weight was 187,000. The preparation of the poly-(4-vinylpyridine betaine) used in this work has been described in a previous report.[6]

Kinetic Runs and Interpretation of Data.—Initial rates at 50° were followed by bromide evolution as described previously, making the appropriate correction for the hydrolysis of the C–Br bond[3] in the interpretation of the data. The results were expressed in terms of a second-order rate constant k_2 (l.-equiv.$^{-1}$ min.$^{-1}$). For the reaction of α-bromoacetamide with poly-(methacrylic acid) (PMA), k_2 was defined by

$$R_T - R_H = k_2(\mathrm{BAc})C_p\alpha' \qquad (2)$$

where R_T is the total observed rate of bromide evolution, R_H the rate due to hydrolysis, (BAc) the α-bromoacetamide concentration, C_p the normality of the PMA and α′ its degree of ionization, which was obtained from the degree of neutralization α and the hydrogen ion concentration by $\alpha' = \alpha + (\mathrm{H}^+)/C_p$. With the dicarboxylic acids kinetic runs were carried out in solutions in which the fraction of neutralized carboxyls was $^1/_4$ or $^3/_4$, so that the reagent served also to buffer the solution. The results of the two runs were interpreted by

$$R_T - R_H = (\mathrm{BAc})[k_2'(\mathrm{HA}^-) + 2k_2''(\mathrm{A}^=)] \qquad (3)$$

where (HA^-) and $(\mathrm{A}^=)$ are the concentrations of the singly and doubly ionized acid, while k_2' and k_2'' are second-order rate constants characterizing ionized carboxyl groups in these two species.

With bromoacetic acid, second-order rate constants were calculated for reactions of the bromoacetate ion from the difference of the total observed rate of bromide evolution R_T

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(1) Taken in part from a thesis submitted by H. Ladenheim in partial fulfillment of the requirements for a Ph.D. degree, June, 1958.

(2) Financial assistance of this study by the Office of Ordnance Research, U. S. Army, and by a grant of the Monsanto Chemical Co. are gratefully acknowledged.

(3) H. Ladenheim, E. M. Loebl and H. Morawetz, THIS JOURNAL, **81**, 20 (1959).

(4) A study of M. L. Bender and Y-L. Chow (*ibid.*, **81**, 3929 (1959)) is concerned with a similar problem involving the reaction of two bifunctional small molecules, *o*-nitrophenyl hydrogen oxalate and 2-aminopyridinium ion.

(5) E. v. Gerichten, *Ber.*, **15**, 1251 (1882).

(6) H. Ladenheim and H. Morawetz, *J. Polymer Sci.*, **26**, 251 (1957).

and a blank R_A which contained in addition to the hydrolytic rate the reaction of un-ionized bromoacetic acid, assumed to have the same rate constant as α-bromoacetamide.

Results and Discussion

The reaction of carboxylic acid anions with bromoacetate and chloroacetate was first investigated by Dawson and his collaborators,[7] who showed that it proceeds by the pathway

$$RCOO^- + XCH_2COO^- \longrightarrow RCOOCH_2COO^- + X^- \quad (4a)$$

$$RCOOCH_2COO^- + H_2O \longrightarrow RCOOH + HOCH_2COO^- \quad (4b)$$

We restricted our study to the initial reaction rate so as to avoid the kinetic complications resulting from the attack of the glycolate ion formed in (4b) on the C–Br bond.

In principle, the action of carboxylate groups of a polycarboxylic acid could differ from the behavior of monofunctional reagents for two reasons: (1) Since the effective acidity of the carboxyl groups attached to a polymer decreases sharply with an increasing degree of ionization,[8] the nucleophilic power of the carboxylate groups could increase if the reaction obeys the Brønsted relation.[9] (2) The reactivity of the carboxylate groups of the polymer may differ from that of monocarboxylic acid anions if there is an energetic interaction between the polymer and the second reagent.[10] Such reactions may involve not only long-range coulombic forces acting on charged reagents[3] but also hydrogen-bonding or the "hydrophobic bond."[11] All these effects should be subject to variation with the degree of ionization of the polymer.

Although the reaction rates of various carboxylic acid anions with bromoacetate and chloroacetate were correlated by Smith[12] with the use of the Brønsted relation, the suggested proportionality of the rate constants on the inverse 0.2 power of the acid dissociation constants suggests that the reactions are rather insensitive to the base strength of the carboxylate. In addition, the correlation is not very reliable, *e.g.*, acetate and formate are equally reactive, although they differ by a factor of ten in basicity.

TABLE I

REACTION OF α-BROMOACETAMIDE (BAc) AND BROMOACETATE (BA^-) WITH DICARBOXYLIC ACIDS AT 50°[a]

Acid[b]	$10^3 \cdot (HA^-)$	$10^3 \cdot (A^=)$	$10^3 \cdot$ (BAc)	$10^7 R_T$	$10^7 R_H$	$10^3 k_2'$	$10^3 k_2''$
Glutaric	50	..	2.32	4.83	0.87	3.41	..
Glutaric	36.7	36.7	2.38	10.7	.89	3.41	3.9
Fumaric	25.1	..	2.38	2.34	.89	2.43	..
Fumaric	26.8	27.3	2.42	5.66	.90	2.43	2.4
Maleic	50.2	..	2.42	2.21	.90	1.08	..
Maleic	37.0		2.48	9.10	.94	1.08	3.9
Maleic	11.4	45.6	2.63	11.2	.98	1.08	4.1
			$10^3 \cdot (BA^-)^c$				
Glutaric	24.0	..	2.40	3.19	2.62	0.47	
Glutaric	36.6	36.7	2.57	3.88	2.97		0.25
Maleic	51.4	..	1.30	2.48	2.49	0	
Maleic	40.0	32.7	2.57	2.50	2.46		0

[a] Ionic strength 0.148. [b] The pK values of the acids (ref. 13) are: glutaric, pK_1 4.32, pK_2 5.42; fumaric, pK_1 3.02, pK_2 4.46; maleic, pK_1 1.91, pK_2 6.27. [c] The concentration of the ionized species was calculated from the stoichiometric concn. and the pH assuming a pK of 2.95 for bromoacetic acid.

Reaction with Dicarboxylic Acids.—Before considering the results obtained with a polymeric acid, it will be appropriate to consider the reaction rate constants observed with singly and doubly ionized dicarboxylic acids listed in Table I. It will be noted that with glutaric and fumaric acid, carboxylate groups act almost independently of one another in their reaction with α-bromoacetamide, so that the doubly ionized acid is very nearly twice as reactive as the singly charged anion. The ratios of the first and second ionization constant of these two acids are 12 and 28, respectively,[13] so that after making allowance for the statistical factor of 4[14] we obtain a rather small difference in the basicities of the carboxylates in the singly and doubly ionized species. Only with maleic acid, in which the first ionization constant is 23,000 times as large as the second one[13] would Smith's correlation[12] predict an increase in the reactivity of the carboxylates in the doubly ionized acid by the appreciable factor of 5.6 in reasonable agreement with our observed ratio of 3.7. It is also not unexpected that the reaction of the carboxylates with bromoacetate, involving an interaction of two negatively charged species, is considerably slower than the α-bromoacetamide reaction. The singly ionized glutaric acid reacts one-eighth as rapidly with bromoacetate as with bromoacetamide, which is similar to results obtained by Dawson and Dyson[7] who found the rate of the attack of a carboxylate on bromoacetate to be one-eighth as fast as the rate of attack on the un-ionized acid. Addition of singly and doubly ionized maleate produced no significant increase of bromide liberation from bromoacetate. This may be accounted for by the low basicity of the singly ionized species and by the strong repulsion of bromoacetate from the two closely spaced carboxylates of the doubly ionized maleic acid.

Reaction with Partially Ionized Poly-(methacrylic Acid).—The second-order reaction rate constants obtained with partially ionized poly-(methacrylic acid) as the nucleophile are listed in Table II. With the exception of one run, the ionic strength was kept at the relatively high value of 0.148, so that long-range electrostatic effects were largely swamped by the high counter-ion concentration.[15] The effective dissociation constant of the carboxyl groups defined by $K_a = a_{H^+}\alpha'/(1 - \alpha')$ declined, as a result, only from 8.0×10^{-6} to 1.5×10^{-6} as α' was increased from 0.12 to 0.65.

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[7] H. H. Dawson and N. B. Dyson, *J. Chem. Soc.*, **49**, 1133 (1933); H. H. Dawson, E. R. Pycock and G. F. Smith, *ibid.*, 517 (1943).

[8] J. T. Overbeek, *Bull. soc. chim. Belges*, **57**, 252 (1948); A. Katchalsky and J. Gillis, *Rec. trav. chim.*, **68**, 879 (1949).

[9] J. N. Brønsted, *Chem. Revs.*, **5**, 322 (1928); J. N. Brønsted and K. Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[10] H. Morawetz and E. W. Westhead, Jr., *J. Polymer Sci.*, **16**, 273 (1955).

[11] W. Kauzmann, "The Mechanism of Enzyme Action," ed. W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, Md., 1954, p. 71.

[12] G. F. Smith, *J. Chem. Soc.*, 521 (1943).

[13] Birger Adell, *Z. physik. Chem.*, **A185**, 161 (1939).

[14] B. Bjerrum, *ibid.*, **106**, 219 (1923).

[15] J. J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948); A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).

TABLE II

REACTION OF α-BROMOACETAMIDE WITH POLY-(METHACRYLIC ACID) AT 50°

μ	10^3C_P	α'	pH	$10^6 \cdot K_a$	$10^3 \cdot$ (BAc)	10^7R_T	10^7R_H	$10^2 k_2$
0.148	9.07	0.01	2.78		2.48	0.96	0.94	..
.148	9.07	.12	4.24	8.0	2.44	1.95	.91	3.9
.148	9.07	.21	4.83	3.9	2.38	2.25	.89	3.0
.148	9.07	.35	5.25	3.0	2.44	2.47	.91	2.0
.148	9.07	.50	5.34	4.8	2.42	2.60	.90	1.5
.002	9.07	.50	6.24	0.6	2.30	2.39	.84	1.5
.148	18.1	.50	5.52	3.0	2.32	4.08	.87	1.5
.148	9.07	.65	6.08	1.5	2.42	2.61	.90	1.2

Three aspects of the results should be emphasized: (1) The rate constants are generally higher, by a factor ranging from 4 to 10, than the corresponding rate constants involving carboxylate groups of the dibasic acids. (2) The reactivity of the carboxylate groups attached to the polymeric chain decreases sharply with increasing degree of ionization. (3) There is no change in the reactivity of half-ionized poly-(methacrylic acid) on reducing the ionic strength from 0.148 to 0.002, although the dilution of the counter-ions results in an eightfold reduction of K_a. This shows, in agreement with previous results, that changes in the basicity of the carboxylate groups have a negligible effect on their reactivity with α-bromoacetamide.

The relatively high reactivity of the polymer indicates that portions of the macromolecule other than the carboxylate attacking the C–Br bond participate in stabilizing the transition state by interaction, *e.g.*, with the amide group of α-bromoacetamide, while no such coöperative effects play a significant role with the dicarboxylic acid anions. This difference in behavior is not difficult to account for: If one carboxylate of, *e.g.*, doubly ionized glutaric acid attacked the C–Br bond of α-bromoacetamide while the other was engaged in hydrogen-bonding with the amide function, a 10-membered ring would result which is known to have a very low probability. On the other hand, if the C–Br bond is attacked by a carboxylate group of PMA, the amide function will find itself within the swollen polymer coil in a region of very high local carboxylate concentration and although the probability of chelate formation with any given carboxylate will be small, the aggregate probability of chelation *with any one of them* will be quite high. This effect has been demonstrated previously in a case where chelate rings formed easily with a polymeric reagent, although the smallest possible ring size contained 20 atoms.[16]

The decrease in the reaction rate constant with increasing ionization of the polymer may be taken as an indication that bromoacetamide associates more strongly with the un-ionized polymer, but the physical situation is too complex to expect a simple relation between k_2 and α'. In this context we may draw attention to anomalies in the titration curve of poly-(methacrylic acid) which have been interpreted as due to drastic changes in the solvation of the chain during the initial stages of its ionization.[17]

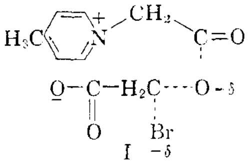
Reaction with 4-Methylpyridine Betaine and Poly-(4-vinylpyridine Betaine).—The results obtained in the reaction of α-bromoacetamide and bromoacetate ion with 4-methylpyridine betaine and poly-(4-vinylpyridine betaine) are listed in Table III. Although the carboxyl in pyridine betaine is very acidic (betaines having generally pK values below 2[18]), it was expected that the reaction with bromoacetate would be fairly rapid due to the electrostatic interaction of the quaternary nitrogen with the carboxylate of the bromoacetate as represented in I

TABLE III

REACTION OF BROMOACETATE (BA⁻) AND α-BROMOACETAMIDE (BAc) WITH 4-METHYLPYRIDINE BETAINE (MPB) AND POLY-(4-VINYLPYRIDINE BETAINE) (PVPB AT 50°)

		(Milliequiv. per liter)			(Moles-l.-min.$^{-1}$)		
μ	pH	(Betaine)	(BAc)	(BA$^-$)[a]	$R_T \times 10^7$	$R_A \times 10^1$	10^3k_2
			MPB				
0	5.75	17.5	3.19	..	1.25	1.40	..
0.148	5.48	17.3	3.21	..	1.25	1.22	..
.003	4.80	20.0	..	3.36	3.23	3.30	..
.148	5.70	16.1	..	3.40	3.23	3.23	..
			PVPB				
0	3.99	6.35	2.22	..	2.49	0.81	11.9
0.148	4.18	6.35	2.28	..	2.11	0.85	8.7
.002	3.60	6.35	..	2.06	3.89	2.48	10.8
.148	3.69	6.35	..	2.24	3.22	2.41	5.7

[a] See footnote *c* of Table I.



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On the other hand, with a large number of the betaine units held in close proximity to each other by the backbone of a polymer chain, the high local concentration of dipolar ions should lead to a high effective dielectric constant[19] and thus slow down the bromine displacement reaction which leads to a dispersal of charge in the transition state.[20]

It was found, however, that 4-methylpyridine betaine failed to produce with either bromoacetate or α-bromoacetamide a significant increase in the rate of bromide formation above that due to hydrolysis, while an appreciable reaction rate was observed in both cases with poly-(4-vinylpyridine betaine). The relatively high values of R_A preclude an exact comparison of the relative reactivity of the polymer and its low molecular weight analog, but it is clear from the data that the betaine groups of the polymer must be more reactive by at least a factor of about 30. Since very similar results were obtained with the charged bromoace-

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(16) H. Morawetz and E. Sammak, *J. Phys. Chem.*, **61**, 1357 (1957).

(17) A. M. Kotliar and H. Morawetz, THIS JOURNAL, **77**, 3692 (1955).

(18) O. Weider, *Ber.*, **68**, 263 (1935); C. Gustafson, *ibid.*, **77B**, 66 (1944).

(19) J. Wyman, *Chem. Revs.*, **19**, 213 (1936).

(20) D. Straup and E. J. Cohn, THIS JOURNAL, **57**, 1794 (1935).

tate and the uncharged bromoacetamide, no long-range electrostatic forces can be involved. It must be concluded that both reagents are being concentrated in the region occupied by the polymer since they are better solvating agents than water. This effect apparently more than compensates for that to be expected due to the concentration of dipolar groups.

Conclusions.—The results of this investigation show that uncharged reagents may react with functional groups of polyelectrolytes at rates differing substantially from those characterizing monofunctional or bifunctional analogs. This phenomenon is probably the result of a concentration of the low molecular weight reagent in the region occupied by the swollen polymer coil. In the poly-(vinylpyridine betaine) reaction this seems to be due to mutual attraction of the hydrophobic residues, while the high reaction rates with poly-(methacrylic acid) appear to be a consequence of a coöperative effect involving interaction of several groups of the polymer with the second reagent. Although this is formally analogous to the presumed principle of enzyme action, it must be emphasized that the enhancement of the reaction rate reported in the present study represents a relatively minor effect.

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BROOKLYN 1, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

N-Bromosuccinimide. I. Allylic Bromination, a General Survey of Reaction Variables[1-3]

BY HYP J. DAUBEN, JR., AND LAYTON L. MCCOY[4]

RECEIVED DECEMBER 31, 1958

The effect of environmental factors (oxygen, light), reactant impurities (water, hydrogen bromide, bromine, hydroperoxides) and added substances of potential catalytic or inhibitory activity on the course and the relative reaction times of the reaction of N-bromosuccinimide (NBS) with cyclohexene in refluxing carbon tetrachloride has been investigated. Successive removal of reactant impurities and of environmental factors leads to increasingly longer reaction times and ultimately to very slow allylic bromination and increased bromine addition, presumably due to bromine formed by the reaction of NBS with hydrogen bromide eliminated thermally from the allyl bromide product. Initiation of the usual preparative allylic brominations is attributable to allyl hydroperoxides, inadvertently present in the alkene due to prior autoxidation. Comparative reaction times, using cyclohexene with or without its hydroperoxide, for runs with and without added substances have shown that bromanil, picric acid, *s*-trinitrobenzene and iodine function as inhibitors or retarders and that three classes of compounds act as accelerators: (a) known radical generators (azo-bis-isobutyronitrile, benzoyl peroxide, tetralyl and cyclohexenyl hydroperoxides); (b) bromine generators with NBS (bromine, hydrogen bromide, water, ethanol, thiophenol); (c) *t*-amines (triethylamine, pyridine). From effectivity and reactivity orders it is evident that (i) retarders-inhibitors act on the chain-carrying succinimidyl radicals, (ii) known radical sources initiate the reaction by thermal primary dissociation, except for hydroperoxides, which probably also show radical-induced decomposition and oxidation–reduction decomposition with NBS, (iii) bromine, alone or from its congeners, thermally or photochemically yields bromine radicals to catalyze the reaction, and (iv) *t*-amines accelerate the reaction in the absence of peroxides by an oxidation–reduction decomposition reaction with NBS and in the presence of peroxides additionally by an oxidation–reduction decomposition reaction with the hydroperoxide. Definition of the mechanism of action of *t*-amines with NBS provides rational explanation of the earlier antagonistic report (Braude and Waight) of predominant bromine addition to alkenes. In light of new evidence, the mechanism of the allylic bromination reaction must involve different initiation and termination reactions from those proposed by Bloomfield. In its simplest form, initiation results from thermal or photochemical dissociation of initiators to radicals that react with NBS or alkene to produce the propagation radicals, propagation involves a chain reaction of succinimidyl radicals with alkene and of allyl radicals with NBS, the former probably being rate-determining, and termination presumably occurs by the interaction of two succinimidyl radicals to produce not the coupling product, bis-N-succinimidyl, but instead other stable products, possibly succinimide and acryl isocyanate.

Since 1942, when Ziegler and co-workers[5] first reported that N-bromosuccinimide (NBS) could be used to effect allylic brominations of alkenes, many papers concerned with NBS, N-chlorosuccinimide (NCS) and related compounds have been published, and several review articles summarizing these findings have appeared.[6] Most of these publications have dealt with synthetic applications of these reagents. Some have involved studies of certain aspects of the mechanism of side-chain (benzylic) chlorination or bromination,[7] and others have obtained certain results, usually incidental to other objectives,[8] bearing on the mechanism of allylic bromi-

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(1) Presented in part before the 118th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1950 (Abstracts, p. 11-N).

(2) Taken from the Ph.D. Thesis of Layton L. McCoy, University of Washington, 1951.

(3) Supported in part by research contract No. N8-onr-52007 with the Office of Naval Research, U. S. Navy.

(4) Predoctoral Fellow, Atomic Energy Commission, 1950–1951.

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(6) (a) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); (b) W. Ringli, "Bromierungen mit Bromsuccinimid," Leeman, Zurich, 1948; (c) T. D. Waugh, "NBS, Its Reactions and Uses," Boulder, Colo., Arapahoe Chemicals, Inc., 1951; (d) N. P. Buu-Hoi, *Record Chem. Prog.*, **13**, 30 (1952); (e) R. Oda and M. Nomura, *Kagaku*, **8**, 428 (1953); (f) T. Kubota, *ibid.*, **10**, 555 (1955).

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(8) (a) M. G. Ettlinger, Ph.D. Thesis, Harvard University, 1945; *cf.* ref. 6a; (b) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944); (c) H.