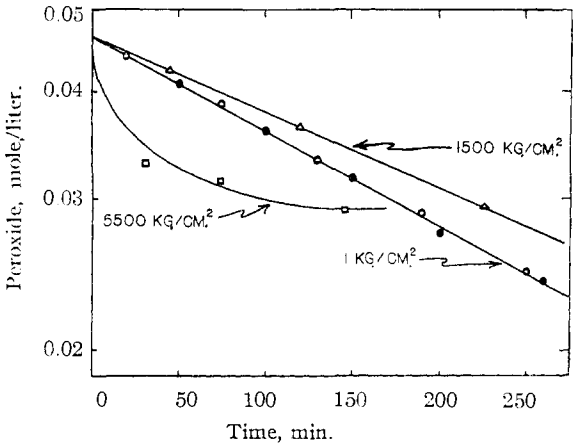

Fig. 3.—Effect of pressure on the decomposition of benzoyl peroxide in acetophenone containing 0.3 molar methyl methacrylate: solid circles, atmospheric pressure run in the presence of 0.3 molar styrene.

striking change in the decomposition of benzoyl peroxide occurs as shown by the curves in Fig. 2 and 3. The reaction rate is now faster than at atmospheric pressure and increases rapidly with pressure. While experimental points are somewhat erratic, particularly at higher pressures, the process appears to be higher than first order. Since we find it hard to conceive of a high-order non-radical process setting in under pressure, we believe that our results indicate the onset of a fast induced chain decomposition of the peroxide. The products of this process have not been determined, so we can say little about its exact nature at present. However, the fact that it occurs equally well in the presence of 0.3 molar methyl methacrylate and also has been noted in allyl acetate[7] indicates that it is not interrupted by unsaturated molecules acting as radical traps as is the case with at least some of the chain decompositions of benzoyl peroxide at atmospheric pressure.[9]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

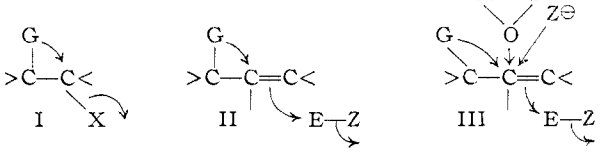
Neighboring Groups in Addition. V.[1] The Benzamido Group in 3-Benzamidopropene[2]

BY LEON GOODMAN AND S. WINSTEIN

RECEIVED APRIL 3, 1957

The neighboring benzamido group participates effectively in the process of addition of bromine to unsaturated amides. Oxazolinium bromides are major products from addition of bromine to 3-benzamidopropene and 3-*p*-methoxybenzamidopropene in chloroform, methanol or acetic acid as solvent. Neighboring benzamido participation competes with that of solvent or bromide. Since solvent participation depends on solvent nucleophilicity, it is important in methanol and negligible in acetic acid. Bromide participation with resulting dibromide formation can be minimized by use of low reagent concentrations in the addition reaction. It can be eliminated conveniently by the use of N-bromosuccinimide as the positive bromine donor. With N-bromosuccinimide in acetic acid, where solvent participation is negligible, essentially quantitative yields of oxazoline are obtained.

The close analogy between participation of a neighboring group G in nucleophilic substitution I and participation of the same group in electrophilic olefin addition II has been pointed out previously.[2a]



The primary OH and OAc groups in allyl alcohol and acetate, respectively, fail to participate during bromine or chlorine addition in methanol or water as solvent.[3] On the other hand, the *t*-OH group in α,α-dimethylallyl alcohol participates to an easily detectable extent in bromine addition, while the *t*-alkoxide ion group ($-O^{\ominus}$) gives essentially exclusive participation in bromine addition to α,α-dimethylallyl alcohol.[4] These observations, as well as others in connection with neighboring carbon,[1,4] are in qualitative agreement with expectations based on a general correlation[1-4] between the incidence or importance of neighboring group participation in addition processes and the size of driving forces due to participation in nucleophilic substitution.[5]

Since 2-benzamido-1-cyclohexyl *p*-toluenesulfonate[2a,6a] and 2-benzamido-1-ethyl toluenesulfonate[6b] and bromide[6c] solvolyze very much more rapidly than the corresponding acetoxy derivatives, we can expect the benzamido group to participate in electrophilic olefin addition to a greater extent than the acetoxy neighboring group. More specifically, 3-benzamidopropene offers a more favorable opportunity to observe participation during bromine addition than does allyl acetate. The present paper is concerned with such a study.

3-Benzamidopropene.—Bergmann,[7,8] who studied

(1) Paper IV, S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

(2) Some of the material of this paper was presented in summary form: (a) S. Winstein, L. Goodman and R. Boschan, THIS JOURNAL, **72**, 2311 (1950); (b) S. Winstein, L. Goodman and R. Boschan, p. 436 of Abstracts, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept., 1951.

(3) S. Winstein and L. Goodman, THIS JOURNAL, **76**, 4368 (1954).

(4) S. Winstein and L. Goodman, *ibid.*, **76**, 4373 (1954).

(5) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

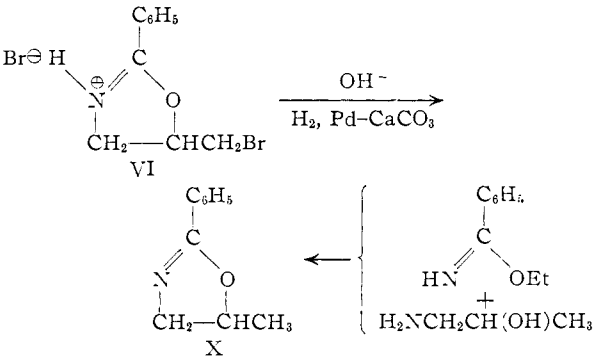
(6) (a) S. Winstein and R. Boschan, *ibid.*, **72**, 4669 (1950); (b) R. Glick, Thesis, U.C.L.A., 1954; (c) F. L. Scott, R. E. Glick and S. Winstein, *Experientia*, **13**, 183 (1957).

(7) M. Bergmann and E. Brand, *Ber.*, **54**, 1645 (1921).

(8) M. Bergmann, F. Dreyer and F. Radt, *ibid.*, **54**, 2139 (1921).

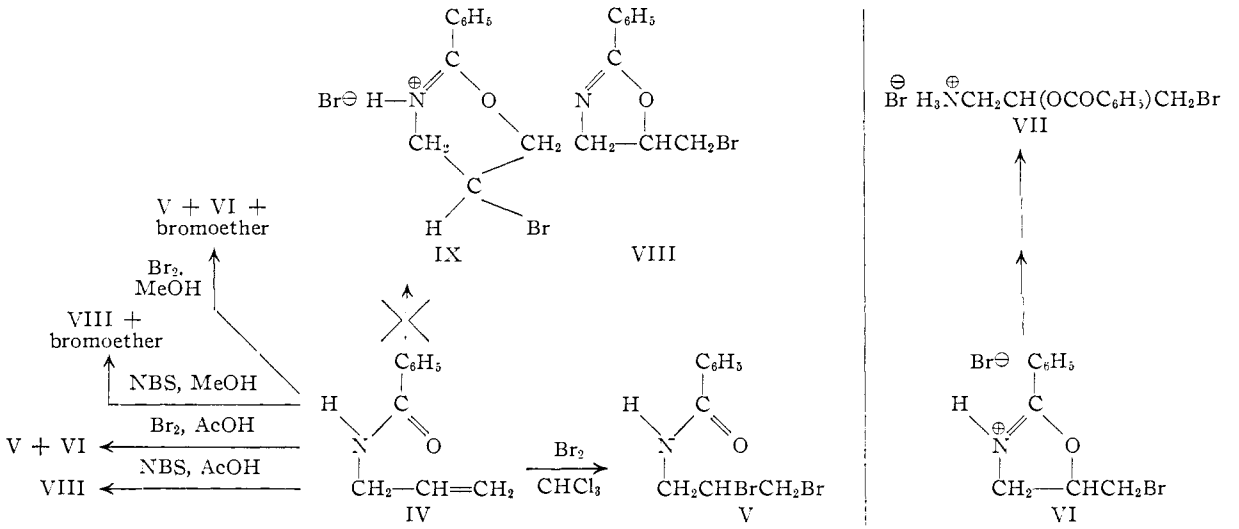
the chlorination and bromination of 3-benzamidopropene (IV) in chloroform, treated the initial reaction product with water and obtained two substances, the simple dihalide V and the hydrohalide salt of the 3-halo-2-benzoyloxypropylamine (VII). He observed[8] that although dibromide V was converted to VII by heating with water or by heating at 100°, it was completely stable under the conditions for the isolation of VII. He reasoned that the dibromide V could not be an intermediate in the formation of VII. Instead he suggested that the formation of VII proceeded *via* 2-phenyl-5-bromomethyloxazolinium bromide (VI).

In the present work, the oxazolinium salt VI was isolated as a major product in the bromination of 3-benzamidopropene (IV) in chloroform, methanol and acetic acid as solvents. The compound gave an equivalent weight in the Volhard titration within 0.3% of the theoretical value and also consumed an equimolar quantity of standard sodium hydroxide. It was converted to the oxazolinium picrate and to the free oxazoline VIII, all three compounds giving the proper carbon and hydrogen analytical values. The possibility was entertained that the salt, represented as oxazolinium salt, was actually the six-membered oxazine IX as a result of O-6 instead of O-5 closure.[9] However, hydrogenolysis with the aid of a palladium catalyst, yielded 5-methyl-2-phenyloxazoline (X). The picrate of the hydrogenolysis product proved to be identical with that of an authentic specimen of oxazoline X prepared from ethyl iminobenzoate[10,11] and 1-amino-2-propanol.



zamido group, solvent and bromide ion may be gained from inspection of the compositions of the isolated products from the addition reactions under different conditions. The data in Table I bring out clearly the dependence of the product composition on the nucleophilicity of the solvent and on the reagent concentration level employed in the addition reaction.

When the bromine addition was performed in the relatively nucleophilic methanol solvent, there was produced a substantial amount of oily bromoether, the product of addition of the elements of methyl hypobromite, to the benzamidopropene IV. On the other hand, in the relatively weakly nucleophilic acetic acid solvent, formation of a bromoacetoxy addition product was not observed.



When high concentrations of bromine and benzamidopropene IV were employed in the addition reaction, the prevailing concentration of oxazolinium bromide VI tended to be high, thus favoring intervention of bromide ion in the addition process with resultant production of dibromide V. This was true both in methanol and acetic acid solvents, as is brought out in Tables I and II. By reducing the concentration level employed in the addition reaction, it was possible to eliminate or reduce very markedly the formation of dibromide in methanol and acetic acid solvents, respectively.

By employing N-bromosuccinimide (NBS) as the positive bromine donor, it was possible more conveniently to eliminate formation of dibromide

Just as in substitution, where neighboring group participation competes with participation by solvent or by added solutes, so in addition processes the neighboring group G competes with solvent molecules (SOH) or solutes (Z^-) for attack on carbon.[3] This competition is symbolized in III. Some idea of the competition between the neighboring ben-

(9) The symbolism employed is explained elsewhere.[6c] O-5 denotes closure of a 5-membered ring, the oxygen atom being the atom in the complex neighboring group which closes the ring.

(10) D. F. Elliot, *J. Chem. Soc.*, 589 (1949).

(11) W. S. Johnson and E. N. Schubert, THIS JOURNAL, **72**, 2187 (1950).

TABLE I

SUMMARY OF PRODUCTS OF ADDITION REACTIONS

Reagent[a]	Solvent	Yield, % Oxazoline	Dibromide	Bromo-ether
3-Benzamidopropene				
1.56 *M* Br_2	$CHCl_3$	42	55	
0.97 *M* Br_2	MeOH	51	28	20
.025 *M* Br_2	MeOH	71		30
.97 *M* NBS[b]	MeOH	61		31
.94 *M* Br_2	AcOH	45	49	
.025 *M* Br_2	AcOH	82	7	
.62 *M* NBS	AcOH	86		
3-*p*-Methoxybenzamidopropene				
0.97 *M* Br_2	MeOH	55	28	17
.025 *M* Br_2	MeOH	76		24
.93 *M* NBS	MeOH	70		22
.67 *M* NBS	AcOH	96		

[a] The concentration of reagent, which is listed for comparison purposes, is calculated from the total amount of reagent added during the reaction and the total volume of solvent employed. [b] N-Bromosuccinimide.

V from benzamidopropene IV. When NBS was employed in acetic acid solvent, in which solvent intervention is also negligible, an excellent yield of pure oxazoline VIII was obtained (Table I).

The results obtained make it evident that the tendency for neighboring benzamido participation in addition to benzamidopropene IV is sufficiently pronounced, that simple precautions to minimize solvent and halide ion intervention suffice to ensure complete control of the addition process by the neighboring benzamido group.

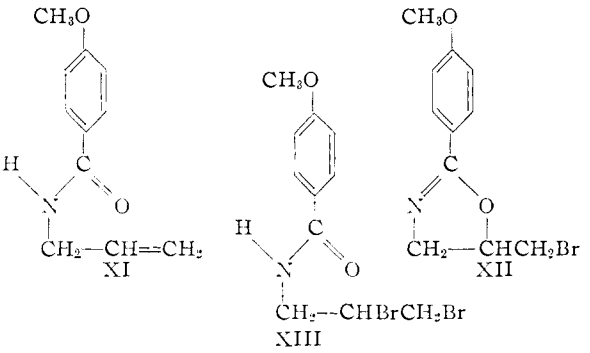
TABLE II

EFFECT OF BROMINE CONCENTRATION ON YIELD OF OXAZOLINE SALT IN METHANOL

3-Benzamidopropene [Br_2], *M*	Fraction ionic bromide	3-*p*-Methoxybenzamidopropene [Br_2], *M*	Fraction ionic bromide
0.0101	1.00	0.0101	1.00
.0533	0.97	.0517	1.03
.110	.92	.105	0.99
.192	.84	.194	.96
.233	.83	.296	.93
.346	.79		
.440	.71	.403	.85
.552	.41	.532	.41
.588	.39		
.857	.37	.819	.39
.0122[a]	.93[a]		

[a] In acetic acid as solvent.

3-*p*-Methoxybenzamidopropene.—The *p*-methoxy derivative of 3-benzamidopropene (XI) was subjected to several addition reactions, the results obtained being analogous to those for 3-benzamidopropene (IV). As brought out in Table I, oxazoline XII or its hydrobromide was obtained in yields of 55–96%, depending on conditions. Also obtained were the dibromide XIII, while in methanol some bromo-ether was obtained as an oil with the correct C,H analysis. The melting point behavior of the dibromide XIII was interesting, since it resolidified after first melting and remelted at the melting point of the oxazolinium bromide. Apparently, the dibromide ionizes above its melting point, giving rise to the isomeric oxazolinium bromide.



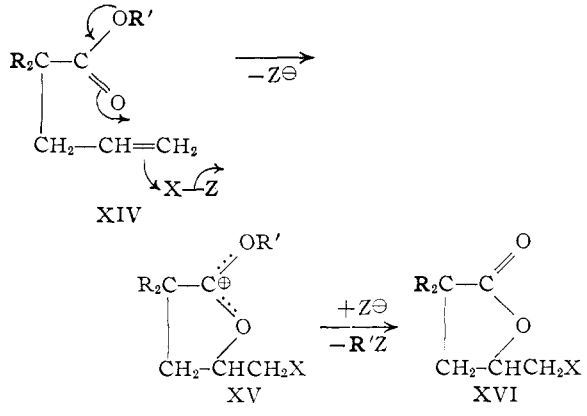
Because of the presence of the electron-supplying methoxyl group in 3-*p*-methoxybenzamidopropene (XI), one would expect neighboring acylamino participation to be favored in competition with solvent and halide ion intervention in the addition process. Tables I and II show that there are small but definite differences between the results with 3-benzamidopropene (IV) and 3-*p*-methoxybenzamidopropene (XI) which are in the expected direction. The latter gave higher yields of oxazoline derivative under all the conditions used, and titration experiments summarized in Table II also showed less tendency for bromide ion intervention.

Other Complex Neighboring Groups.—It is clear that the benzamido and *p*-methoxybenzamido groups participate effectively in addition processes and that such participation is understandable on the basis of the analogy between electrophilic olefin addition and nucleophilic substitution.

Recently Scott, Glick and Winstein[6c] reported that the sequence of decreasing rate constants for neutral solvolysis of a series of compounds G CH_2CH_2Br was: G = C_6H_5CONH > $C_6H_5NHCONH$ > EtNHCOO > CH_3COO. Applying these data to participation in bromine addition it would be predicted that both N-allylurethan and N-allylurea would yield smaller proportions of heterocycles resulting from participation than did N-allylbenzamide (3-benzamidopropene). Actually, Bergmann[8] did note that addition of bromine to N-allylurethan yielded only the simple dibromide. The situation with N-allylurea is not clear. Andreasch[12] reported that the addition of bromine to aqueous or alcoholic N-allylurea gave quantitatively the simple dibromide, while Rundqvist[13] reported that the addition of iodine to N-allylurea gave a diiodo compound that was a salt. It would obviously be necessary to repeat the above additions under controlled irreversible conditions comparable to those used in the present work before any comparison would be valid. It is of interest that the additions of chlorine,[14] bromine[15,16] and iodine[15,16] to N-allylthiourea have been reported to give salts. This is an indication of the superiority of thioamido over analogous amido groups for neighboring group participation.

(12) R. Andreasch, *Monatsh.*, **5**, 33 (1884).
(13) C. Rundqvist, *J. Chem. Soc.*, **76**, 16 (1899).
(14) J. Gadamer, *ibid.*, **70**, 414 (1896).
(15) R. Maly, *Z. Chem.*, 258 (1869).
(16) A. E. Dixon *J. Chem. Soc.*, **69**, 17, 851 (1896.)

Recently Arnold and co-workers[17] studied the participation of another complex[6] neighboring group, the carboalkoxy group, in halogen and pseudo-halogen addition to certain unsaturated esters XIV. These yielded bromo- and iodolactones XVI as major products in a number of cases.



This effect had been observed previously by Craig and Witt[18] in bromine additions. Analogous lactonization in additions of 2,4-dinitrobenzenesulfenyl chloride to unsaturated acids has been reported by de Moura Campos.[19] The participation of the carboalkoxy group in the addition process is analogous to that of the benzamido group in the present work, except that this produces an unstable intermediate XV instead of an isolable salt.

Experimental[20]

3-Benzamidopropene (IV) and 3-*p*-Methoxybenzamidopropene (XI).—These amides were prepared by reaction of allylamine with the appropriate acid chloride in aqueous sodium hydroxide solution. The N-benzoyl compound boiled at 125–128.5° (1 mm.) and melted at 22.5° [reported, b.p. 173–174° (14 mm.),[21] m.p. 17°[22]]. The N-anisoyl compound melted at 43–44.2° after crystallization from ligroin–benzene.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85. Found: C, 68.89; H, 6.89.

Reaction of IV with Bromine in Chloroform.—A solution of 10.2 g. (0.063 mole) of dry bromine in 20 ml. of chloroform was added to a stirred solution of 10.2 g. (0.063 mole) of IV in 20 ml. of chloroform over a 50-minute period, maintaining the temperature at 0°. A further 27 ml. of chloroform was added to facilitate stirring since precipitation occurred during the addition. The mixture was allowed to warm to room temperature during 30 minutes and 100 ml. of dry ether was added. The precipitate (18.5 g.) was filtered and Volhard titration showed it to consist of 44.7% of the oxazoline salt VI and 55.3% of the dibromide V. Evaporation of the filtrate in vacuum gave 1.34 g. of V which was crystallized from methanol; m.p. 129–130.5° (reported 129.5–130°[23] and 135°[8]).

A portion of the mixture of V and VI was suspended in dilute, aqueous sodium hydroxide solution and, after filtration, the residue was triturated with warm ether. Addition of an ethereal picric acid solution to the ether extract gave the oxazoline picrate which was crystallized from methanol; m.p. 168–169.5°.

Anal. Calcd. for $C_{16}H_{12}O_8N_4Br$: C, 40.95; H, 2.79; N, 11.94. Found: C, 41.12; H, 2.79; N, 12.13.

Reaction of IV with Bromine in Dry Methanol.—The quantities used were 10.1 g. (0.063 mole) of bromine, 10.1 g. (0.063 mole) of IV and 65 ml. of dry methanol and the conditions of reaction were similar to those in chloroform. By filtration, 4.63 g. of solid (77.2% of V and 22.8% of VI) was recovered. Addition of dry ether to the filtrate precipitated 9.18 g. of solid which had equivalent wt. values of 321.5 and 314.7 (neutralization and Volhard titration), indicating a minimum oxazoline salt content (calcd. 321.0) of 98%. A portion of this material was dissolved in methanol and precipitated with dry ether to give a solid, m.p. 147.5–148°.

Anal. Calcd. for $C_{10}H_{11}ONBr_2$: C, 37.41; H, 3.45. Found: C, 37.58; H, 3.40.

The filtrate from the second precipitate (9.18 g.) was evaporated *in vacuo* and 5.7 g. of an oily solid resulted. This was shown to contain about 35% of V and about 4% of the hydrolysis product from VI, 3-bromo-2-benzoyloxypropylamine hydrobromide (VII), m.p. 186–188°. The rest of the 5.7 g. was a yellow oil considered to be bromo-ether.

When the addition was repeated using 1.61 g. (0.01 mole) of bromine, 1.62 g. (0.01 mole) of IV and 400 ml. of dry methanol, 2.30 g. of solid, m.p. 146–147°, equivalent wt. by Volhard titration, 320.3, was obtained along with 0.87 g. of an oil considered to be bromo-ether. Only traces of V could be obtained from this oil.

The dibromide V, shaken with dry methanol for one hour at 25°, gave rise to no ionic halogen as determined by the Volhard titration.

Reaction of IV with Bromine in Dry Acetic Acid.—A solution of 5.05 g. (0.031 mole) of IV in 33 ml. of dry acetic acid was cooled to 15° and 5.0 g. (0.031 mole) of bromine was added during 10 minutes. After warming to 20° during 30 minutes the mixture was filtered from 2.55 g. of solid which contained 14.4% of VI. Addition of dry ether to the filtrate gave 4.41 g. of solid, m.p. 146.5–147.5°, which contained 94% of VI. Evaporation of the filtrate gave 2.50 g. of V, recovered in 3 crops, m.p. 122.5–128°.

A repetition of the reaction using 0.01 mole each of bromine and IV in 400 ml. of dry acetic acid gave 2.60 g. of VI, m.p. 144–146°, equivalent wt. 319.0, on precipitation by ether, and 0.58 g. of solid on evaporation of the filtrate. This latter solid yielded 0.21 g. of V and 0.03 g. of 3-bromo-2-benzoyloxypropylamine hydrobromide (VII).

That VI did not isomerize to V under the conditions of addition was demonstrated by shaking a suspension of VI in dry acetic acid for 1.5 hours at room temperature. Precipitation of the picrate gave a 92% recovery of the salt.

2-Phenyl-5-bromomethyloxazoline (VIII).—An aqueous solution of VI was mixed with a small excess of an aqueous sodium acetate solution. Ether extraction, followed by drying and evaporation of the extract, gave an oil which was evaporatively distilled at 0.1 mm. (bath temperature 110–115°) to give a distillate which crystallized on standing. Crystallization from petroleum ether gave a solid, m.p. 33.5–34.8°.

Anal. Calcd. for $C_{10}H_{10}ONBr$: C, 50.02; H, 4.20. Found: C, 49.93; H, 4.10.

Reaction of N-Bromosuccinimide (NBS) with IV in Dry Methanol.—A mixture of 5.53 g. (0.031 mole) of NBS, 5.0 g. (0.031 mole) of IV and 33 ml. of dry methanol was stirred at room temperature for 2 hours, a clear solution resulting. The methanol was evaporated *in vacuo* to a small volume (5–10 ml.) and 200 ml. of dry ether was added. After filtration of 2.43 g. of succinimide the ether was evaporated at room temperature, a yellow oil resulting. This oil was extracted with several portions of boiling petroleum ether, 2.69 g. of oil failing to dissolve. The residue from the evaporation of the petroleum ether extract was dissolved in dry ether and to this solution was added an ethereal solution of 5.02 g. (0.031 mole) of picric acid. A picrate, 8.81 g., m.p. 166–167°, m.p. 167.5–169° when mixed with authentic oxazoline picrate, was obtained. The 2.69 g. of yellow oil could not be induced to crystallize and chromatography on activated alumina gave no solid material so the oil was considered to be bromo-ether.

Reaction of NBS with IV in Dry Acetic Acid.—A mixture of 2.78 g. (0.016 mole) of NBS, 2.52 g. (0.016 mole) of IV and 26 ml. of dry acetic acid was stirred at room tempera-

(17) (a) R. T. Arnold, M. de Moura Campos and K. L. Lindsay, THIS JOURNAL, **75**, 1044 (1953); (b) R. T. Arnold and K. L. Lindsay, *ibid.*, **75**, 1048 (1953).

(18) P. N. Craig and I. H. Witt, *ibid.*, **72**, 4925 (1950).

(19) M. de Moura Campos, *ibid.*, **76**, 4480 (1954).

(20) Melting and boiling points are uncorrected.

(21) P. Kay, *Ber.*, **26**, 2848 (1893).

(22) M. Bergmann, F. Radt and E. Brand, *ibid.*, **54**, 1645 (1921).

(23) W. J. Gensler, THIS JOURNAL, **70**, 1843 (1948).

ture for 3 hours. The acetic acid was evaporated under vacuum and 100 ml. of dry ether was added to the residue. After filtration of 0.78 g. of succinimide, an ethereal solution of 3.59 g. (0.016 mole) of picric acid was added to the filtrate, yielding 6.36 g. (86.4%) of the picrate, m.p. 167–170°.

2-Phenyl-5-methyloxazoline (X). (a) By **Hydrogenolysis.**—A mixture of 1.61 g. (0.005 mole) of VI, 0.60 g. (0.015 mole) of sodium hydroxide, 1.5 g. of catalyst (2% palladium-on-calcium carbonate) and 50 ml. of dry methanol was shaken at room temp. with hydrogen at 23 p.s.i. for 5 hours, during which time there was no hydrogen absorption. At the end of 8 hours, however, 0.012 mole of hydrogen had been absorbed. This induction period was noted in all similar hydrogenations. The solution was neutralized with Dry Ice and filtered. The methanol was evaporated and the salts were extracted with boiling chloroform. Evaporation of the chloroform left a non-crystallizable liquid which was dissolved in dry ether and added to an ethereal solution of 1.10 g. (0.005 mole) of picric acid, yielding 0.60 g. (33%) of a yellow solid, m.p. 162–169°, m.p. 168.5–171° after two crystallizations from methanol, m.p. undepressed by mixing with the synthetic sample of 5-methyl-2-phenyloxazoline picrate (*cf.* below), mixed m.p. with 2-phenyl-5-bromomethyloxazoline picrate 150–158°.

Anal. Calcd. for $C_{16}H_{14}O_8N_4$: C, 49.23; H, 3.62; N, 14.36. Found: C, 49.46; H, 3.65; N, 14.32.

(b) By **Synthesis.**—Ethyl iminobenzoate hydrochloride, 1.74 g. (0.01 mole), was dissolved in alcohol-free chloroform and the solution was shaken with aqueous sodium hydroxide solution. The chloroform layer was dried with potassium carbonate and 0.76 g. (0.01 mole) of 1-amino-propanol-2 was added. Ammonia was evolved when the solution was refluxed (12 hours). Then the chloroform was evaporated and the residue was dissolved in dry ether. Addition of an ethereal solution of 2.29 g. (0.01 mole) of picric acid precipitated a yellow solid (3.1 g., 80% yield), m.p. 165–170°, m.p. 170–171.6° (reported[21] 167°) after crystallization from methanol, mixed m.p. with the picrate of the hydrogenation product 169.5–171.2°.

Reaction of XI with Bromine in Dry Methanol.—A solution of 12.0 g. (0.063 mole) of XI in 65 ml. of dry methanol was chilled to −3° and 10.1 g. (0.063 mole) of bromine was added, with stirring, during 30 minutes. After stirring for another hour, while the temperature rose to 20°, the mixture was filtered and the precipitate (5.25 g.) was washed with cold, dry methanol. The solid showed essentially no ionic halogen (Volhard method) and a portion of it was crystallized from methanol to give an analytical sample which showed no ionic halogen and melted partially at about 135°, resolidified and remelted at 182–183°. This was the dibromide XIII.

Anal. Calcd. for $C_{11}H_{13}O_2NBr_2$: C, 37.63; H, 3.73. Found: C, 37.70; H, 3.97.

Addition of 500 ml. of dry ether to the filtrate and washings precipitated 12.07 g. of a white, water- and methanol-soluble solid which, by Volhard titration, had an equivalent weight of 350.4 (calcd. 351.1). A portion of this solid was dissolved in dry methanol and precipitated with dry ether to give a solid, m.p. 181–182.5°.

Anal. Calcd. for $C_{11}H_{13}O_2NBr_2$: C, 37.63; H, 3.73. Found: C, 37.49; H, 3.68.

A solution of the salt was made basic with sodium hydroxide solution and the ether extract of this solution was added to an ethereal picric acid solution giving a yellow solid, m.p. 174.5–175.5° after crystallization from methanol.

Anal. Calcd. for $C_{17}H_{15}O_9N_4Br$: C, 40.90; H, 3.01; N, 11.22. Found: C, 40.93; H, 3.22; N, 10.96.

Evaporation, *in vacuo*, of the filtrate from the second precipitate, yielded 0.74 g. of XIII and 3.48 g. of a semi-solid material. A further 0.2 g. of XIII was obtained from the latter but the remaining material could not be crystallized and evaporative distillation at 0.1 mm. resulted in decomposition. The oil was assumed to be bromo-ether.

When the addition was carried out in dilute solution using 1.91 g. (0.01 mole) of XI, 1.60 g. (0.01 mole) of bromine and 400 ml. of dry methanol, there was obtained 2.65 g. (75.5%) of oxazolinium salt, m.p. 181–182°, equivalent weight 351.9. Evaporation in vacuum of the filtrate yielded 0.74 g. of semi-solid material. This was dissolved in chloroform and passed through a 45 × 20 mm. column of activated alumina. The eluate was an oil.

Anal. Calcd. for $C_{12}H_{16}O_3NBr$: C, 47.69; H, 5.39. Found: C, 48.20; H, 5.82.

2-*p*-Methoxyphenyl-5-bromomethyloxazoline (XII).—The procedure used for 5-bromomethyl-2-phenyloxazoline (VIII) was followed. Evaporation of the dried ether extract gave a solid, m.p. 91.1–91.5° after crystallization from ligroin.

Anal. Calcd. for $C_{11}H_{12}O_2NBr$: C, 48.53; H, 4.48. Found: C, 48.80; H, 4.58.

Reaction of NBS with XI in Dry Methanol.—A mixture of 5.0 g. (0.026 mole) of XI, 4.67 g. (0.026 mole) of NBS and 28 ml. of dry methanol was stirred at room temperature until all solids had dissolved (1.25 hours). The solution was evaporated *in vacuo* and the residue was treated with dry ether, filtration removing some succinimide. The ether was evaporated to about 50 ml. and more succinimide was filtered, the filtrate then being taken to dryness. The residue was extracted with three 25-ml. portions of hot ligroin, an oil remaining undissolved. The extract, on chilling, deposited a white solid (3.0 g.), m.p. 91–92° after three crystallizations from ligroin. The insoluble oil was extracted with several portions of hot ether, a sizable portion failing to dissolve. The ether extract was mixed with an ethereal solution of 3.0 g. (0.013 mole) of picric acid, and 3.7 g. of picrate, m.p. 174.5–176.5°, was precipitated. The remaining oil, 1.74 g. (22% considered as bromo-ether), could not be induced to crystallize.

Reaction of NBS with XI in Dry Acetic Acid.—A mixture of 3.82 g. (0.02 mole) of XI, 3.56 g. (0.02 mole) of NBS and 30 ml. of dry acetic acid was stirred at room temperature for 2.5 hours. The acetic acid was removed at the water-pump and the residue was extracted with five 50-ml. portions of boiling ligroin. This extract was filtered and the filtrate concentrated to about 100 ml. Chilling in ice precipitated 5.11 g. of solid, m.p. 75–85°, m.p. 86.5–89° after crystallization from ligroin. The residue from the extraction was extracted with boiling absolute ether to give, after addition of an ethereal picric acid solution, 0.15 g. of picrate, m.p. 157–169°.

Determination of Percentage Ionic Halogen Produced at Various Bromine Concentrations.—Bromine was added to a tared glass ampoule, and the ampoule was sealed and reweighed. It was then placed in a solution of a known weight of amide in a known volume of dry methanol. The mixture was cooled in ice-water, and the ampoule was broken beneath the surface of the solution. The solution was shaken at room temperature until the bromine color had disappeared; then an aliquot was removed and added to water. Ionic halide was determined by Volhard titration.

In these titration experiments excess amide was used, the disappearance of the bromine color requiring about three minutes at 25°. At high bromine concentrations the dibromide precipitated from the reaction mixtures, and the aliquots taken for titration were removed from the supernatant liquid after the precipitate settled. The data for the dilute solutions are the most reliable. The results of the titration experiments are summarized in Table II.

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