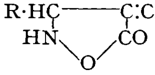
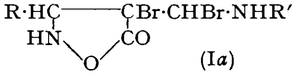
696. iso*Oxazolones. Part IV.** *The Bromination of Arylaminomethylene*iso*oxazolidones. A New Selective Anion-precipitant.*

By G. Shaw.

The reaction of 3-methyl-4-*p*-toluidinomethylene*iso*oxazolid-5-one (I; R = Me, R′ = *p*-tolyl) with bromine gave the hydrobromide of 3-amino-1 : 2-dibromo-1-*p*-toluidinobut-2-ene (II*a*) which was readily dehydrobrominated to 3-amino-2-bromo-1-*p*-tolyliminobut-2-ene (III*a*). Similar compounds were obtained from (I; R = Me, R′ = Ph) but not from (I; R = Ph, R′ = *p*-tolyl). With the potassium salts of a number of simple acids, the hydrobromide of (III*a*) gave insoluble crystalline salts in dilute, neutral and acidic solution. The properties of some of the salts were examined and the precipitant compared with known anion-precipitants, including nitron which was in general more sensitive but less selective.

During an investigation of arylaminomethylene*iso*oxazolidones (*J.*, 1951, 1017; 1952, 3428), it was observed that addition of bromine to a solution of 3-methyl-4-*p*-toluidinomethylene*iso*oxazolid-5-one (I; R = Me, R′ = *p*-tolyl) in acetic acid gave carbon dioxide and an immediate orange-yellow precipitate. With care, a compound (*A*) could be crystallised from acetic acid but when its solution in that solvent was boiled for a short time a second substance (*B*) was obtained. Hydrolysis of *A* or *B* with dilute hydrochloric acid gave ammonia, *p*-toluidine, and bromoacetone, and this, in conjunction with analytical data, indicated that *A* and *B* are hydrobromides of the bases (II*a*) and (III*a*) respectively the reaction *A* ⟶ *B* being a dehydrobromination. That the compounds were salts was confirmed by treatment with sodium hydroxide solution which in each case gave the same base, namely (III*a*). Hydrolysis of the impure precipitate *A* also gave, in addition to the above-mentioned compounds, a small amount of 2 : 6-dibromo-*p*-toluidine which suggested the presence, in the mixture, of (II*c*) although this could not be isolated, and at the same time indicated a source of hydrogen bromide for the main reaction, in which (I*a*) would be an intermediate.


(I)


(I*a*)

$NH_2{\cdot}CMe{:}CBr{\cdot}CHBr{\cdot}NHR$

(II*a*; R = *p*-tolyl)

(II*b*; R = Ph)

[II*c*; R = 2 : 6-dibromo-*p*-tolyl (Me = 4)]

$NH_2{\cdot}CMe{:}CBr{\cdot}CH{:}NR$

(III*a*; R = *p*-tolyl)

(III*b*; R = Ph)

An aqueous solution of the sparingly soluble hydrobromide of (III*a*) gave crystalline precipitates in dilute, neutral and acidic solution with a number of anions, including nitrate, iodide, perchlorate, chromate, thiocyanate, and picrate, but not with chloride, nitrite, sulphate, phosphate, acetate, or oxalate. Organic bases which form water-insoluble salts with simple anions are relatively uncommon and include nitron (cf. Cope and Barab, *J. Amer. Chem. Soc.*, 1917, **39**, 504), di-(α-naphthylmethyl)amine (Rupe and Becherer, *Helv. Chim. Acta*, 1923, **6**, 674, 885; Konek, *Z. anal. Chem.*, 1934, **97**, 416), and 2-diethylamino-1-phenethyl *p*-nitrobenzoate (Marvel and du Vigneaud, *J. Amer. Chem. Soc.*, 1924, **46**, 2095, 2661). Some comparative approximate minimum anion concentrations required for precipitation are given in the Table. Our hydrobromide and the *p*-nitrobenzoate are more selective in their action, but much less sensitive, than nitron.

The precipitate from the reaction between potassium iodide and the hydrobromide of (III*a*) contained potassium and is apparently a double salt of the reactants. It had approximately the same solubility as the hydriodide of (III*a*), and was precipitated as

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* Part III, *J.*, 1952, 3428.

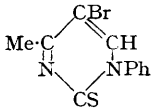
brownish-yellow needles at anion concentrations >0·1N but as a deep blue-black form in more dilute solution; the latter, when heated, reverted to the brown modification.

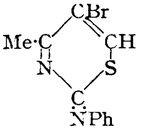
The thiocyanate of (III*a*) could not be isomerised to the corresponding thiourea; an ethanolic solution of the salt, however, when left at room temperature for several days gave a small amount of a bright yellow substance to which no simple structure could be assigned. The reaction between (III*a*) and phenyl *iso*thiocyanate gave a similar yellow compound, analysis of which, however, indicated it to be derived from the expected thiourea by loss of *p*-toluidine; it may be formulated as the thiopyrimidone (IV), rather than (V) since it failed to give aniline when boiled with dilute hydrochloric acid.

Minimum anion concentration (N) *for precipitation at* 20°.

Anion	(III*a*)	*p*-Nitrobenzoate	Nitron	Anion	(III*a*)	*p*-Nitrobenzoate	Nitron
NO_3	0·01	0·005	0·0001	I	0·0005	0·01	0·0005
ClO_4	0·0025	0·0025	0·0001	CNS	0·025	—	0·001

(IV)





(V)

Bromination of (I; R = Me, R′ = Ph) gave, in a similar manner, salts of (II*b*) and (III*b*), and the latter product formed salts which were slightly more soluble than those of (III*a*). Treatment of (I; R = Ph, R′ = *p*-tolyl) with bromine in acetic acid, in a single attempt to obtain a more sensitive compound, failed to yield a precipitate or any obvious signs of reaction even after several days at room temperature; when the solution was warmed, a vigorous reaction occurred, but only 2 : 6-dibromo-*p*-toluidine (Me = 4) was isolated.

EXPERIMENTAL

3-*Amino*-1 : 2-*dibromo*-1-p-*toluidinobut*-2-*ene* (II*a*).—3-Methyl-4-*p*-toluidinomethylene*iso*oxazolid-5-one (5 g.) in acetic acid (100 ml.) was treated with a solution of bromine (4 ml.) in acetic acid (25 ml.). Carbon dioxide was liberated (barium hydroxide solution) and an immediate orange-yellow precipitate appeared; 3-*amino*-1 : 2-*dibromo*-1-p-*toluidinobut*-2-*ene hydrobromide* (8 g.) separated from warm acetic acid (the solution must not be boiled) as orange-yellow prisms, m. p. 238° (decomp.) (Found: C, 32·45; H, 3·5; N, 6·75. $C_{11}H_{14}N_2Br_2,HBr$ requires C, 31·8; H, 3·65; N, 6·75%); the high value for carbon may be due to the presence of a small amount of the dehydrobrominated material.

3-*Amino*-2-*bromo*-1-p-*tolyliminobut*-2-*ene* (III*a*).—The dibromo-compound (8 g.) was boiled with acetic acid (400 ml.) until a clear solution resulted; when cooled, the solution deposited red crystals (4·5 g.); 3-*amino*-2-*bromo*-1-p-*tolyliminobut*-2-*ene hydrobromide* separated from acetic acid as reddish-orange cruciform prisms or from water as yellow prisms, m. p. 198° (decomp.) (Found: C, 39·2; H, 4·15; N, 8·45. $C_{11}H_{13}N_2Br,HBr$ requires C, 39·5; H, 4·2; N, 8·4%); a further quantity (1 g.) was obtained on concentration. The hydrobromide (1 g.) was dissolved in water (150 ml.), and the solution made alkaline with 2N-sodium hydroxide, to give a cream precipitate; 3-*amino*-2-*bromo*-1-p-*tolyliminobut*-2-*ene* (0·6 g.) separated from light petroleum as very pale yellow plates, m. p. 98° (Found: C, 52·15; H, 5·0; N, 11·1. $C_{11}H_{13}N_2Br$ requires C, 52·2; H, 5·2; N, 11·05%). The hydrobromide (1 g.) was boiled under reflux with 2N-hydrochloric acid (20 ml.) for 30 min. and the resulting clear solution distilled until the volume was about 10 ml. The distillate was strongly lachrymatory and with an excess of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid gave, overnight, bromoacetone 2 : 4-dinitrophenylhydrazone, yellow needles (from ethanol), m. p. and mixed m. p. 123°. When the residual hydrolysis solution was basified with sodium hydroxide solution there was an odour of ammonia; extraction with ether gave a base characterised as the benzoyl derivative, m. p. 157—158° not depressed when mixed with *N*-benzoyl-*p*-toluidine. A similar hydrolysis carried out on the first-mentioned bromination product gave, in addition to *p*-toluidine, ammonia, and bromoacetone, a small amount of solid which appeared in the distillate and crystallised from ethanol–water as colourless needles, m. p. 69° (Found: C, 31·8; H, 2·75; N, 5·3. Calc. for

$C_7H_7NBr_2$: C, 31·7; H, 2·65; N, 5·3%), not depressed on admixture with 2 : 6-dibromo-*p*-toluidine.

3-*Amino*-1 : 2-*dibromo*-1-*anilinobut*-2-*ene* (II*b*).—4-Anilinomethylene-3-methyl*iso*oxazolid-5-one (2·5 g.) in acetic acid (50 ml.) was treated with bromine (2 ml.) in acetic acid (15 ml.); an immediate yellow microcrystalline precipitate was filtered off rapidly; the filtrate when kept for a short time deposited yellow prisms (3 g.), m. p. 200° (decomp.). The compound could not be recrystallised satisfactorily but was probably 3-*amino*-1-*anilino*-1 : 2-*dibromobut*-2-*ene acetate* (Found : C, 37·95; H, 4·15; N, 7·45. $C_{10}H_{12}N_2Br_2,C_2H_4O_2$ requires C, 37·9; H, 4·25; N, 7·35%).

3-*Amino*-2-*bromo*-1-*phenyliminobut*-2-*ene* (III*b*).—The acetate (1 g.), when boiled with acetic acid, similarly gave 3-*amino*-2-*bromo*-1-*phenyliminobut*-2-*ene hydrobromide* (0·3 g.) as yellow prisms (from acetic acid), m. p. 184—185° (decomp.) (Found : N, 8·8. $C_{10}H_{11}N_2Br,HBr$ requires N, 8·75%). Hydrolysis of the hydrobromide or the acetate with hydrochloric acid gave ammonia, aniline, and bromoacetone.

Bromination of 3-*Phenyl*-4-p-*toluidinomethylene*iso*oxazolid*-5-*one*.—The *iso*oxazolidone (1 g.) and bromine (0·5 ml.) were mixed in acetic acid; no obvious reaction occurred when the mixture was left at room temperature for 3 days. Heating caused a vigorous reaction, with liberation of hydrogen bromide; the clear solution obtained when treated with excess of water gave 2 : 6-dibromo-*p*-toluidine, m. p. and mixed m. p. 68—69°.

Salts of 3-*Amino*-2-*bromo*-1-p-*tolyliminobut*-2-*ene*.—A saturated solution of the hydrobromide with 0·1N-solutions of the potassium salts of a number of acids gave the results recorded. The *nitrate monohydrate* separated from water as pale yellow needles, m. p. 205° (decomp.) (Found : C, 39·75; H, 4·55; N, 12·3. $C_{11}H_{13}N_2Br,HNO_3,H_2O$ requires C, 39·5; H, 4·2; N, 12·55%), the *perchlorate* as cream prisms (from water), m. p. 245° (decomp.) (Found : C, 37·35; H, 3·9; N, 8·1. $C_{11}H_{13}N_2Br,HClO_4$ requires C, 37·6; H, 4·0; N, 8·0%), and the *thiocyanate* as pale yellow needles (from water), m. p. 160° (decomp.) (Found : C, 46·0; H, 4·4; N, 13·4. $C_{11}H_{13}N_2Br,HCNS$ requires C, 46·15; H, 4·5; N, 13·45%). The salt gave a blood-red colour with ferric chloride. The product of reaction of the hydrobromide and potassium iodide was obtained as brown needles from 0·1N-solutions and as deep blue hair-like needles from more dilute solution; the blue substance was converted into the brown by heating it at 100° for 10 min. The *substance* separated from ethanol–water as brownish-yellow needles, m. p. 185° (decomp.) (Found : C, 26·95; H, 2·8; N, 5·55. $C_{11}H_{13}N_2Br,HBr,KI$ requires C, 26·4; H, 2·8; N, 5·6%). This (0·05 g.) was suspended in ethanol (1 ml.), and 2N-sodium hydroxide (1 drop) was added to give a clear solution from which excess of water precipitated 3-amino-2-bromo-1-*p*-tolyliminobut-2-ene (0·02 g.), m. p. and mixed m. p. 97—98° The *iodide hemi-hydrate* (from the hydrobromide and hydriodic acid or sodium iodide) separated from water as yellow needles, m. p. 183° (decomp.) (Found : C, 33·8; H, 3·75; N, 7·3. $C_{11}H_{13}N_2Br,HI,\frac{1}{2}H_2O$ requires C, 33·8; H, 3·85; N, 7·2%).

Attempted Rearrangement of the Thiocyanate.—The thiocyanate (0·5 g.) in ethanol (5 ml.), left at room temperature for 2 days, gave a bright yellow solution; addition of water precipitated a *substance* (0·1 g.) which separated from ethanol–water as yellow needles, m. p. 185° (decomp.) (Found : C, 35·25; H, 3·9; N, 7·55%).

Anion :		Ppt.		Anion :		Ppt.	
Nature	N	Neutral	Plus 1 drop of N-HCl	Nature	N	Neutral	Plus 1 drop of N-HCl
NO_3	0·1	Immediate	Immediate	ClO_4	0·01	5 Min.	15 Min.
NO_3	0·025	10 Min.	1 Hr.	ClO_4	0·0025	Overnight	Overnight
NO_3	0·01	Overnight	None	ClO_4	0·001	None (cloudy)	None
I	0·01	Immediate	Immediate	CNS	0·1	Immediate	Immediate
I	0·001	2 Hr.	2 Hr.	CNS	0·025	Overnight	Overnight
I	0·0005	Overnight	Overnight	CNS	0·01	None	None
I	0·0001	None (cloudy)	None				

Reaction of (III*a*) *with Phenyl* iso*Thiocyanate*.—The base (0·5 g.) and phenyl *iso*thiocyanate (0·5 g.) were mixed in ether (10 ml.) and left overnight. A crystalline solid separated, together with a red gum. The solid (0·1 g.) crystallised from benzene–light petroleum as yellow prisms, m. p. 140° (decomp. with resolidification to a brown material, m. p. 300°) and may be 5-*bromo*-4-*methyl*-1-*phenyl*-2-*thiopyrimidone* (Found : C, 46·5; H, 3·1; N, 9·5. $C_{11}H_9N_2BrS$ requires C, 46·95; H, 3·2; N, 9·95%). It was soluble in concentrated mineral acid solutions and was recovered unchanged after being boiled with 5N-hydrochloric acid for a few min.

Sensitivity of the Anion Tests.—The tests were carried out by treating 5 ml. of the anion solution (K^+ or a common cation) with 0·5 ml. of a saturated solution of the hydrobromide of (III*a*) at 20°; the rate of precipitation and the sensitivity were increased by cooling the solutions.

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