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EFFECT OF INORGANIC SALTS ON BROMINATIONS WITH N-BROMOSUCCINIMIDE[1, 2]

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In a previous study (1) concerning polar effects in brominations with N-bromosuccinimide, it was found that very erratic results were obtained with commercially available samples of N-bromosuccinimide. Only when pure reagent that had been carefully recrystallized from boiling water was used could consistent results be obtained. Since the most likely impurity in the N-bromosuccinimide was inorganic salts, a comprehensive investigation of their effects on the bromination was undertaken.

For these studies a series of reagents containing various amounts of inorganic salts were prepared. A reagent containing 80% N-bromosuccinimide and 20% potassium bromide was prepared by the treatment of a solution of potassium hydroxide and succinimide in 33% methanol with bromine. The amount of the N-bromo compound was determined iodometrically and the amount of the potassium salt was determined by ashing with perchloric acid. A similar reagent containing 82% N-bromosuccinimide with 18% sodium bromide was made using sodium hydroxide. When pure methanol was used as the solvent for the reaction, a reagent composed of 61% N-bromosuccinimide and 39% potassium bromide was formed. The use of 15% methanol as the solvent produced a reagent composed of 86% N-bromosuccinimide and 14% potassium bromide.

When these reagents were used in bromination of olefins rather surprising results were obtained. These results are summarized in Table I.

When methyl crotonate was brominated with pure N-bromosuccinimide, an 83% yield of the γ-bromo derivative was obtained. However, when the reagent containing 20% potassium bromide was used, the only isolated product was the methyl 2,3-dibromobutyrate in a 44% yield while none of the γ-bromo derivative was detected.

With pure N-bromosuccinimide, cyclohexene (I) gave a 50% yield of 3-bromocyclohexene (II) and 6% of 1,2-dibromocyclohexane (III). With the reagent containing 20% potassium bromide, the proportion of the two products was almost reversed; a 13% yield of II and 35% of III were obtained. Similar results were obtained with the reagent containing 18% sodium bromide.

In order to determine the effect of the state of dispersion or degree of mixing of the inorganic salt on the bromination, several reagents were prepared by

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TABLE I

EFFECT OF INORGANIC SALTS ON BROMINATIONS WITH N-BROMOSUCCINIMIDE

Compound[a]	N-Bromosuccinimide		Salt in Reagent[b]		Salt Added[c]		Reaction Time, Hours	Benzoyl Peroxide, Mole	Carbon Tetrachloride	Product	Yield[d]	Boiling Point					n_D^{25}		Olefin Recovered	Succinimide Recovered	Salt Recovered
	Concn., Wt. %	Mole		Wt.-%		Mole						Found		Reported			Found	Reported			
												°C.	mm.	°C.	mm.	Ref.					
									ml.		%								%	%	%
Methyl crotonate	100	0.60	—	—	—	—	1.25	0.04	600	Methyl γ-bromocrotonate	83	84–86	12	83–85	13	5	1.4959	1.498[e](6)	—	96	—
	80	.52	KBr	20	—	—	72	—	680	Methyl α,β-dibromobutyrate	44	58–60	1.5	103	15	7	1.5017		—	50	70
Cyclohexene	100	.41	—	—	—	—		.012	700	3-Bromocyclohexene (II)	50	80–82	15	45–47	10	8			28	85	—
										1,2-Dibromocyclohexane (III)	6	95–107[l]	15	51–57	1	8					
	80	.50	KBr	20	—	—		—		II	13								—	70	90
										III	35										
	82	.50	NaBr	18	—	—		—		II	8								74	70	86
										III	24										
	100	.50	—	—	KBr	0.17		—		II	48								65	91	87
										III	14										
	100	.50	—	—	KCl	.20		—		II	46								—	93	98
										III	24										
	100	.50	—	—	NaBr	.22		—		II	48								52	88	86
										III	—										
Styrene	100	.50	—	—	—	—	192	.04	700	Styrene dibromide (IV)	6	73–74[f]		72–73[f]		9			90	22	—
	86	.52	KBr	14	—	—		—		IV	59								—	—	—
	80	.52	KBr	20	—	—		—		IV	73								—	70	96
	61	.51	KBr	39	—	—		—		IV	81								—	62	86
	100	.56	—	—	KBr[g]	.17		—		IV	16								—	—	—
	100	.52	—	—	KBr[h]	.17		—		IV	35								70	42	92
	100	.46	—	—	KBr	.17		—		IV	63								—	—	—
	100	.46	—	—	KCl	.17		—		IV	65								70	61	80
	100	.44	—	—	KI	.15		—		IV	47								68	38	87

Vinylaceto-nitrile	100	.67	—	—	—	—		.013	500	γ-Bromocrotonitrile (V)	13	88–92	10	73–90	10	10	1.5001	1.4963[i](11)	—	trace	—
										3,4-Dibromobutyronitrile (VI)	23	120–124	10	138.5–139	20	12	1.5165				
	80	.58	KBr	20	—	—		.013	625	V	22								—	94	79
										VI	51										
	61	.58	KBr	39	—	—		—		V	23								60	94	74
										VI	60										
	80	.58	KBr	20	—	—		—[j]		V	15								—	69	95
										VI	64										
Ethyl acrylate	80	.72	KBr	20	—	—	72	—	670	Ethyl α,β-dibromopropionate	3	70–73	5	112	23	13	1.4956	1.5015[k](13)	—	—	—
Benzalacetone	100	.96	—	—	—	—	48	—	750	—	0								90	—	—
	80	.96	KBr	20	—	—	72	—	750	Benzalacetone dibromide	37	119–121[f]		121–124[f]		14			22	—	—

[a] Figures adjusted to 1 mole of compound   Coprecipitated with the N-bromosuccinimide. [c] Salt and N-bromosuccinimide ground together in a mortar except as noted. [d] Based on the N-bromosuccinimide; olefin was always in excess. [e] n_D^{19}. [f] Melting point. [g] Potassium bromide added as large pieces, 2–3 mm. in diameter. [h] Potassium bromide and N-Bromosuccinimide ground separately. [i] n_D^{20}. [j] Trace of *p-tert*-butylcatechol added. [k] n_D^{16}. [l] M.p. −2 to −4°.

grinding various amounts of inorganic salts and N-bromosuccinimide together in a mortar. When cyclohexene (I) was brominated with pure N-bromosuccinimide plus 20% added potassium bromide, a 48% yield of II and a 14% yield of III were obtained. Thus the effect of the mechanically added salt is not as great as the effect of the coprecipitated potassium bromide. Similar effects were noted for the mechanically added potassium chloride and sodium bromide. With the added potassium chloride no evidence was found that the chloride ion was adding to the double bond. Since this work was completed,[2] Braude and Waight (2) reported that when lithium chloride was mechanically added in the bromination of cyclohexene little effect was observed. The yield of II remained unchanged at 30% while the yield of III increased from 12 to 20%. Similarly, addition of potassium chloride produced a 31% yield of II and a 31% yield of III. Addition of the more soluble amines and their derivatives had a more pronounced effect.

When styrene was brominated with pure N-bromosuccinimide only a 6% yield of styrene dibromide (IV) was obtained. However, when the reagent containing 20% potassium bromide was used, a 73% yield of IV was obtained. Only a small additional effect was noted for the reagent containing 39% potassium bromide; an 81% yield of IV was found.

When the concentration of coprecipitated potassium bromide was lowered to 14%, only a 59% yield of styrene dibromide (IV) was obtained. These three runs indicate that there is a correlation between the concentration of the inorganic salt and the amount of addition obtained in the bromination.

In order to determine the relation between the fineness of grinding and intimacy of mixing of the potassium bromide and the N-bromosuccinimide and the course of the bromination, several variations were tried. When styrene was treated with pure N-bromosuccinimide to which 20% of 2- to 3-mm. pieces of potassium bromide had been added, the yield of IV was only 16%. However, the yield of IV increased to 35% if the two reagents were ground separately before they were added to the reaction mixture. If potassium chloride, potassium bromide, or potassium iodide was intimately ground with the N-bromosuccinimide, the yield of IV was further increased to 47 to 65%. In these latter cases no evidence was found that the chloride or iodide ion added to the double bond.

With vinylacetronitrile pure N-bromosuccinimide produced a 13% yield of γ-bromocrotonitrile (V) and a 23% yield of 3,4-dibromobutyronitrile (VI). When the reagent containing 20% potassium bromide was used, a 22% yield of V and a 51% yield of VI were produced. In a similar reaction in which a small amount of *p-tert*-butylcatechol was substituted for the peroxide in order to inhibit the free radical reaction, the yield of VI increased to 64% while the yield of V dropped to 15%. If the reagent containing 39% potassium bromide was used in a reaction with vinylacetonitrile, a 23% yield of V and a 60% yield of VI were isolated.

Although benzalacetone does not react to any appreciable extent with pure N-bromosuccinimide (1, 3), when the reagent containing 20% potassium bromide was used for the bromination, a 37% yield of benzalacetone dibromide was formed.

The exact function of the added inorganic salt is not clear. The salts do, however, promote the ionic addition of bromine to the double bonds in the presence or absence of peroxide or *p-tert*-butylcatechol. No evidence was found for the participation of the added anion in the addition to the double bond. One must conclude that the intimate mixture of the reagent with the potassium bromide polarizes the nitrogen-bromine bond so that the heterolytic cleavage in the ionic reaction can take place more readily. Since these inorganic salts are almost completely insoluble in carbon tetrachloride, the reaction is heterogeneous, with the salts acting either as ion pairs or ionic aggregates that have a powerful surface effect.

In many of these reactions a high yield of succinimide was formed. The source of the hydrogen on the succinimide was not determined. One might assume that potassium bromide might react somehow to form potassium succinimide. However, the potassium succinimide is strongly basic while the reaction mixture was invariably slightly acidic. Although it was previously reported (1) that an added inhibitor, such as *p-tert*-butylcatechol, could serve as the source of this hydrogen, other investigators (3, 4) have also been unable to determine the source of the hydrogen for the formation of succinimide during the addition of bromine to olefins using N-bromosuccinimide.

EXPERIMENTAL[5]

Materials. Pure N-bromosuccinimide. Commercial N-bromosuccinimide was carefully purified by recrystallization from ten times its weight of boiling water to produce material that assayed above 99.3% when reacted with potassium iodide in acetic acid, followed by titration with standard sodium thiosulfate solution.

N-Bromosuccinimide (80%) containing 20% potassium bromide. To a mixture of 200 ml. of methanol and 400 ml. of water was added 65 g. of potassium hydroxide. The solution was cooled to 0° and 99 g. (1 mole) of succinimide was added with vigorous stirring. After any insoluble material was removed by filtration, 160 g. (1 mole) of bromine was added rapidly with stirring. The precipitated N-bromosuccinimide-potassium bromide mixture was removed by filtration, washed with three 100-ml. portions of methanol, and dried over phosphorus pentoxide under a vacuum. The yield was 150 g. The N-bromosuccinimide content was determined iodometrically and the potassium bromide content was determined by ashing with perchloric acid.

N-Bromosuccinimide (61%) containing 39% potassium bromide. The procedure described above for the reagent containing 20% potassium bromide was used with the exception that absolute methanol was substituted for the aqueous methanol.

N-Bromosuccinimide (86%) containing 14% potassium bromide. The procedure described above was used with the exception that a 15% (by volume) aqueous methanol solution was substituted for the 33% (by volume) methanol solution.

N-Bromosuccinimide (82%) containing 18% sodium bromide. To a solution of 40 g. of sodium hydroxide in 100 ml. of water at 0° was added 90 g. of succinimide. The mixture was filtered and 145 g. of bromine was added rapidly to the filtrate. The precipitated reagent was removed by filtration, washed with methanol, and dried over phosphorus pentoxide under a vacuum. The composition was determined as previously described.

Carbon tetrachloride. Carbon tetrachloride was purified by extraction with concentrated sodium hydroxide, concentrated sulfuric acid, dilute sodium bicarbonate solution, and water. It was dried over phosphorus pentoxide and carefully fractionated.

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[5] All melting points are corrected.

The other materials were the highest purity commercial grade available. The organic reagents were purified before use by distillation or recrystallization.

Brominations with N-bromosuccinimide reagents. All brominations were carried out in the usual manner. The experimental details and the results are listed in Table I. All of the dibromides were compared with the product obtained by bromination of the corresponding olefin with elemental bromine. The dibromides of styrene, cyclohexene, and benzalacetone were identified by mixture melting point determinations with authentic samples. A typical bromination is described below.

Bromination of vinylacetonitrile with N-bromosuccinimide (61%) containing 39% potassium bromide. A mixture of 205 g. of 61% N-bromosuccinimide [containing 125 g. (0.70 mole) of N-bromosuccinimide and 80 g. (0.67 mole) of potassium bromide], 80 g. (1.2 moles) of vinylacetonitrile, and 750 g. of carbon tetrachloride was heated under reflux for 14 hours. The reaction mixture was cooled and filtered and the filtrate was fractionated through an 8-inch, helix-packed column to yield 48 g. (60% recovery) of unchanged vinylacetonitrile, 23.5 g. (23% based on the N-bromosuccinimide) of γ-bromocrotonitrile, b.p. 88–92° (10 mm.), n_D^{25} 1.5001 [reported b.p. 73–90° (10 mm.) (10), n_D^{20} 1.4963 (11)]; and 46.4 g. (60% based on the N-bromosuccinimide) of 3,4-dibromobutyronitrile, b.p. 120–124° (10 mm.), n_D^{25} 1.5165 [reported (12) b.p. 138–139° (20 mm.)]

The solid from the above reaction was leached with chloroform to obtain 65 g. (94%) of succinimide, m.p. 122–125°. The chloroform-insoluble residue was leached with 450 ml. of distilled water. This aqueous solution was at *p*H 2. (The original reaction mixture was also acidic.) Evaporation of the aqueous solution produced 59 g. (74%) of potassium bromide.

SUMMARY

The presence of coprecipitated inorganic salts in N-bromosuccinimide reagents greatly increased the amount of addition during bromination reactions. The effect of added inorganic salts was not as large. Since no evidence was found that the anion of the added salt entered into the addition reaction and the reaction mixture invariably remained acidic, it was concluded that the salt aided the heterolytic cleavage of the bromine-nitrogen bond by polarization of that bond.

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