2 - (2,4,6 - Triethylphenyl)ethanol. 2,4,6 - Triethylbenzyl chloride (0.063 mole) was converted to the nitrile and the crude nitrile hydrolyzed as described under the preparation of 2-(*p*-ethylphenyl)ethanol to give 2,4,6-triethylphenylacetic acid (16% yield), m.p. 95–96°. The 2,4,6-triethylphenylacetic acid (0.01 mole) was reduced using lithium aluminum hydride[21] to give 2-(2,4,6-triethylphenyl)ethanol (80% yield), m.p. 39–40°; 3,5-dinitrobenzoate, m.p. 97.5–98.0°.

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DAVIS, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Comparison of *N*-Bromoacetamide and *N*-Bromosuccinimide as Brominating Agents[1]

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A comparison of *N*-bromoacetamide and *N*-bromosuccinimide as brominating agents in reactions which were presumably free radical in type has been carried out especially with reference to their tendencies to give allylic bromination or addition to the double bond. It was found qualitatively that *N*-bromoacetamide showed more tendency toward addition and was the more reactive reagent. *N*-Bromodiacetimide, which closely resembles *N*-bromosuccinimide from the standpoint of electronic configuration but which is more like *N*-bromoacetamide from the standpoint of steric strain, was so reactive it could not be prepared pure. Crude solutions of it reacted with olefins to give bromine addition products as the only ones isolated, but these could have arisen from the reaction with bromine formed by decomposition. An investigation of the fate of the acetamidyl radical during the reaction of *N*-bromoacetamide with styrene to give styrene dibromide showed that when the reactants were carefully mixed so that the reaction proceeded rapidly and smoothly nearly all of the acetamidyl radical could be identified as acetamide. The source of the hydrogen necessary for acetamide formation, at least in some of the cases, must have been either styrene or a brominated product, but no products formed by such hydrogen abstraction could be isolated.

N-Bromoacetamide has been used[2] as a source of bromine atoms for substitution on the allylic position, and N-bromosuccinimide has been developed[3–7] extensively as a brominating agent for allylic positions and aromatic side chains. For each of these *N*-bromo compounds, however, addition of bromine to the double bond has at times been observed under conditions expected to favor free radical reactions. *N*-Bromoacetamide appears to give this type of reaction quite readily.[8,9] In the case of its reaction with styrene the free radical nature of the reaction was especially apparent.[8] Addition with *N*-bromosuccinimide has been observed[10–16] as the main reaction in several cases while in other cases some addition has been observed when substitution was the main reaction.[6,15–19] In several instances there was extensive addition under conditions favorable to free radical reactions.[10–13] In other cases the beneficial effects of antioxidants such as *p-tert*-butylcatechol[15,16] and of halide ion[14,16] in promoting addition reactions have been interpreted in terms of polar mechanisms.

The results of the present investigation are summarized in Table I. In the cases studied *N*-bromoacetamide tended to give addition preferentially and *N*-bromosuccinimide gave the expected allylic bromination where possible. In detail the results of Table I do not always agree with results reported elsewhere. For example, no cyclohexene dibromide was isolated from the reaction with *N*-bromosuccinimide but small amounts have been reported[15–18] under conditions favorable to free radical reactions. No dibromide could be isolated from extended interaction of styrene with *N*-bromosuccinimide in the

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(1) From the Ph.D. Theses of William J. Probst and Robert C. Johnson. Presented before the Organic Division of the American Chemical Society, Cincinnati, Ohio, March, 1955.

(2) Wohl, *Ber.*, **52**, 51 (1919); Wohl and Jaschinowsky, *Ber.*, **54**, 476 (1921).

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

(4) Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(5) Djerassi, *Chem. Rev.*, **43**, 271 (1948).

(6) Ziegler, Spath, Schaaf, Schumann, and Winkelmann, *Ann.*, **551**, 80 (1942).

(7) Waugh, "*N*-Bromosuccinimide, Its Reactions and Uses," Arapahoe Chemicals, Inc., Boulder, Colo., 1951.

(8) Buckles, *J. Am. Chem. Soc.*, **71**, 1157 (1949).

(9) Buckles and Maurer, *J. Org. Chem.*, **18**, 1585 (1953).

(10) Corey, *J. Am. Chem. Soc.*, **75**, 2251 (1953).

(11) English and Gregory, *J. Am. Chem. Soc.*, **71**, 1115 (1949).

(12) Buchman and Howton, *J. Am. Chem. Soc.*, **70**, 2517, 3510 (1948).

(13) Southwick, Pursglove, and Numerof, *J. Am. Chem. Soc.*, **72**, 1600 (1950).

(14) Braude and Waight, *Nature*, **164**, 241 (1949); *J. Chem. Soc.*, 1116 (1952).

(15) Bailey and Bello, *J. Org. Chem.*, **20**, 525 (1955).

(16) Bello, *Univ. Microfilms., Publ.* No. **10050**; *Dissertation Abstr.*, **14**, 1921 (1954).

(17) Park, Gerovich, Lycan, and Lacher, *J. Am. Chem. Soc.*, **74**, 2189 (1952).

(18) Howton, *J. Am. Chem. Soc.*, **69**, 2060 (1947).

(19) Couvreur and Bruylants, *Bull. soc. chim. Belg.* **61**, 253 (1952).

absence of an efficient hydrogen source or of halide ion, but a small yield has been reported[15,16] under such conditions. In another report[20] styrene was listed as being unreactive to *N*-bromosuccinimide.

TABLE I

REACTIONS OF OLEFINS WITH *N*-BROMOAMIDES

Olefin	*N*-Bromoamide[a]	Mole Ratio[b]	Solvent	Type of Bromination	Total Yield (%) Isolated
2-Methyl-2-hexene	NBS[c]	0.5	CCl_4	Allyl[d]	41
	NBA[c]	1.25	CCl_4	Addition	50
	NBD[c]	0.67	CCl_4	Addition	29
Cyclohexene	NBS[e]	0.2	CCl_4	Allyl	58
	NBA[e]	2.0	CCl_4	Addition	47
	NBA[e]	0.25	CCl_4	Allyl	36
	NBD[e]	2.0	$HCCl_3$	Addition	33
Styrene	NBS[f]	1.0	CCl_4	Addition	0
	NBS[g]	1.0	$CHCl_3$	Addition	26
	NBA[c]	2.0	CCl_4	Addition	34
	NBA[c]	2.0	$CHCl_3$	Addition	52
	NBD[c]	2.0	$HCCl_3$	Addition	24
1,3-Diphenylpropene	NBS[h]	0.83	CCl_4	?[i]	0
	NBA[h]	2.0	CCl_4	Addition	23
	NBD[h]	2.0	$HCCl_3$	Addition	10
Isobutylene	NBS[j]	..	$CHCl_3$	?[k]	0
	NBA[j]	..	$CHCl_3$	Addition	42
Ethyl cinnamate	NBS[l]	1.0	$CHCl_3$	Addition	0
	NBA[e]	2.0	$CHCl_3$	Addition	39
Methyl cinnamate	NBA[e]	2.0	$CHCl_3$	Addition	30
Trans stilbene	NBA[e]	2.0	$CHCl_3$	Addition	42
Tolan	NBA[e]	2.0	CCl_4	Addition	32
Benzalacetophenone	NBA[e]	2.0	$CHCl_3$	Addition	57
Phenylacetylene	NBA[e]	2.0	$CHCl_3$	Addition	37

[a] NBS represents *N*-bromosuccinimide; NBA, *N*-bromoacetamide; NBD, crude *N*-bromodiacetimide. [b] Mole ratio of *N*-bromoamide to olefin. [c] In each of these cases the solution was warmed to start the reaction and the olefin or *N*-bromoamide was added slowly enough to maintain the reaction mixture at or below the boiling point. [d] This product consisted of 27% 2-methyl-4-bromo-2-hexene and 14% of a crude dibromo-2-methyl-2-hexene. [e] The solution was boiled under reflux until there was no test for *N*-bromoamide with moist starch-iodide paper. [f] This entry represents the results of a number of experiments in which the solution was boiled under reflux for as long as 4 days and illuminated with an ultraviolet lamp during that period for 22 hrs. At the end of this maximum period of time, a 95% recovery of NBS and a 75% recovery of styrene were made. With shorter reaction periods even more NBS could be recovered. The addition of a small amount of NBA did not initiate any reaction. [g] Ethyl alcohol (10 ml. per 100 ml. of $CHCl_3$) was added before any change took place with the relatively insoluble NBS. [h] The solution was refluxed for from 15 to 30 min. [i] A residue which gave off hydrogen bromide but would not crystallize was formed. [j] Carried out at room temperature under a Dry Ice reflux condenser as isobutylene was bubbled into the solution. [k] The only product other than succinimide charred and decomposed on distillation. [l] This reaction was carried out under reflux under ultraviolet illumination for 3 days. The NBS was recovered in 92% yield.

(20) Kharasch and Priestley, *J. Am. Chem. Soc.*, **61**, 3425 (1939).

When cyclohexene reacted with excess *N*-bromoacetamide the reaction which took place was addition, but with excess olefin substitution was observed as had been reported.[17] With 2-methyl-2-hexene, on the other hand, the reaction was controlled by adding *N*-bromoacetamide a little at a time so that the olefin was in excess but the addition product was obtained. None of the reaction mixtures gave any isolable amounts of 1:1 adducts of the sort that have been reported for the reactions of *N*-bromosulfonamides,[20,21] *N*-haloamides,[6,17] *N*-bromoimides,[6,15,16] or *N*-bromomorpholine[22] with olefinic compounds.

In connection with the addition of bromine the fate of the nitrogen-containing radical is of interest. When *N*-bromosuccinimide has been involved good yields of succinimide have usually been reported.[10-19] In connection with *N*-bromoacetamide some acetamide and sometimes some bisacetamide hydrobromide have been found,[8] but never enough to account for much of the acetamidyl radical. In the present investigation the reaction of *N*-bromoacetamide and styrene was found to give yields of acetamide as high as 65%. When the acetamide was isolated by precipitation as bisacetamide hydrochloride yields as high as 97% were obtained. Such complete accounting for the acetamidyl radical was possible only when the reaction was carried out with just the right degree of control. In one experiment, where the reagents were mixed too fast, for example, the reaction mixture was extracted as completely as possible with water. It was possible to account for 74.5% of the nitrogen in the water-soluble portion and for 21.7% of the nitrogen in the water insoluble portion. Thus, some of the acetamidyl radical itself can be involved in addition to give water insoluble products.

In order to account for the acetamidyl radical forming acetamide it is necessary for a source of hydrogen to be available. In at least some of the experiments with styrene, where there was no hydrogen available from the solvent, this must have been either the styrene or a brominated product. No products resulting from this type of action could be isolated however. A simple dehydrogenation of styrene would be expected to yield phenylacetylene, but this compound reacted with *N*-bromoacetamide to yield what appeared to be its dibromide which should have been isolable had appreciable amounts been present in the reaction mixture. It seems that the dehydrogenation of either styrene or a brominated product was accompanied by some kind of polymerization, but polystyrene was not formed.[8] The presence of other possible hydrogen donors did not change the situation in general. With chloroform or benzene as solvents there was no evidence of dehydrogenation products arising from

(21) Foldi, *Ber.*, **63**, 2257 (1930).

(22) Southwick and Walsh, *J. Am. Chem. Soc.*, **77**, 405 (1955).

the solvent. Stilbene was brominated and triphenylmethane did not react when they were included in the reaction mixture as possible hydrogen sources.

In the case of the reaction of tolan with *N*-bromoacetamide neither the starting olefin nor the dibromide appear to have been likely sources of hydrogen. From this reaction mixture only a 70% yield of bisacetamide hydrochloride could be isolated. In cases such as this some of the acetamide may have acted as a source of hydrogen, but no products resulting from such a reaction could be isolated.

Ethyl alcohol was evidently an effective hydrogen source since the unreactive combination of *N*-bromosuccinimide and styrene reacted when it was present to give 26% of the dibromide. Even better results have been reported with catechol and *tert*-butylcatechol.[15,16]

Qualitatively there was a striking difference in reactivity between *N*-bromoacetamide and *N*-bromosuccinimide especially in the cases of styrene and ethyl cinnamate which could not undergo allylic bromination. In every case, even when *N*-bromosuccinimide reacted quite rapidly, *N*-bromoacetamide reacted faster.

It had been hoped that a comparison of *N*-bromodiacetimide with the other two *N*-bromoamides would throw some light on the differences in reactivity. The results were disappointing, however, since *N*-bromodiacetimide could be prepared only in an impure solution and its reactions may merely be those of the bromine formed from its decomposition. Its tendency to decompose, however, may be significant in itself. Surely it does act more like *N*-bromoacetamide than like *N*-bromosuccinimide. It may be that the reactivity and instability of *N*-bromoacetamide and especially *N*-bromodiacetimide are caused by steric strain on the nitrogen-bromine bond. Such steric strain would not be a factor in the structure of the cyclic *N*-bromosuccinimide. In any event it is quite evident that in general *N*-bromoacetamide is considerably more reactive than *N*-bromosuccinimide.

The difference in the results of the reactions of these two *N*-bromoamides might be explained on the basis of the reaction scheme outlined in equations 1 to 4. This scheme is consistent with the free radical mechanism proposed for substitution reactions by *N*-bromosuccinimide.[23,24] If the nitrogen-bromine bond were weakened, step 1 and those like step 4 would be particularly affected. If step 2 were faster than 3, but a relatively unfavorable equilibrium, a relatively rapid step 4 would allow step 2 to be relatively slow, but still faster than step 3, and, thus, the predominant path, which would lead to bromine addition. At the same time, a relatively slow step 4 would give the irreversible step 3 a chance to compete successfully with the relatively unfavorable equilibrium of step 2 and substitution would predominate. Decreasing the relative amount of the *N*-bromo compound would have the same effect of favoring step 3 over step 2 while an increase would have the opposite effect.

$$>NBr + h\nu \longrightarrow >N\cdot + Br\cdot \qquad (1)$$

$$>C{=}C{-}CH_2^- + Br\cdot \rightleftharpoons >CBr{-}\dot{C}{-}CH_2^- \qquad (2)$$

$$>C{=}C{-}CH_2^- + >N\cdot \longrightarrow >C{=}C{-}\dot{C}H^- + >NH \qquad (3)$$

$$R\cdot + >N{-}Br \longrightarrow RBr + >N\cdot \qquad (4)$$

Thus, if such a scheme were followed *N*-bromosuccinimide would be expected to tend to give substitution and *N*-bromoacetamide to tend to give addition, which results have been observed. In the cases where *N*-bromosuccinimide gave addition step 2 could be an equilibrium favorable enough to compete with step 3 in spite of a slow step 4.

In order to explain the formation of acetamide or succinimide from the addition reaction it is necessary to consider a source of hydrogen ZH_2 entering into the reaction sequence some such way as shown in steps 5 and 6. Such steps in the sequence make available bromine atoms for step 2. The ease with which a step such as 6 would take place would again depend on the reactivity of the *N*-bromo compound. Since two such steps (4) and (6) would be necessary for the addition reaction only reactive *N*-bromo compounds would usually be expected to react effectively in this way:

$$>N\cdot + ZH_2 \longrightarrow >NH + ZH\cdot \qquad (5)$$

$$ZH\cdot + >N{-}Br \longrightarrow >NH + Z: + Br\cdot \qquad (6)$$

EXPERIMENTAL

N-Bromoacetamide. This compound of m.p. 97–103° was prepared as described[8] for an earlier investigation, but most of the *N*-bromoacetamide used was kindly supplied by Araphoe Chemicals, Inc.

N-Bromosuccinimide. This compound was prepared as described[6] by the alkaline bromination of succinimide, but most of the *N*-bromosuccinimide used was kindly supplied by Arapahoe Chemicals, Inc.

N-Bromodiacetimide. In an all glass system freshly prepared phenyl magnesium bromide [from 15.7 g. (0.10 mole) of bromobenzene] in 200 ml. of anhydrous ether was added to a solution of 10.1 g. (0.10 mole) of diacetimide[25] in 150 ml. of anhydrous ether. A white precipitate formed and the reaction mixture became warm. To this suspension 16 g. (0.10 mole) of bromine was slowly added with stirring. A yellowish semisolid formed during the addition. The yellow solution was decanted and most of the ether was removed by distillation. The concentrated solution was filtered and dissolved in 75 ml. of carbon tetrachloride. This solution was then used in the bromination experiments.

An alternative procedure was the same as the procedure described above until the diacetimidomagnesium bromide was precipitated. This was then filtered from the solution

(23) Bloomfield, *J. Chem. Soc.*, 114 (1944).

(24) Dauben, McCoy, and Youngman, meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Sept. 1950, p. 11N.

(25) Polya and Tardrew, *J. Chem. Soc.*, 1081 (1948).

TABLE II

PROPERTIES OF BROMINATION PRODUCTS

Product	Brominating Agent	B.P., °C.	Pressure, Mm.	M.P.[a] °C.	d_4^{20}	n_D^{20}
2,3-Dibromo-2-methylhexane[b]	Br_2	73–75	8	...	1.5068	1.4990
	NBA	73–74	8	...	1.5063	1.4963
	NBD	69–73	5	...	1.5015	1.4980
4-Bromo-2-methyl-2-hexene[c]	NBS	43–44	5	...	1.1679	1.4785
Dibromo-2-methyl-2-hexene[c]	NBS	90–92.5	5	...	1.5269	1.5333
1,2-Dibromocyclohexane[d]	NBA	99–102	13	...	1.780	1.5530
	NBD	93–96	10	...	1.777	1.5521
3-Bromocyclohexene[e]	NBS	73–76	16	...	1.393	1.5300
	NBA	73–74	14–15	...	1.405	1.5279
1,2-Dibromo-1-phenylethane[f]	NBS	..	..	71–72	..	..
	NBA	108–110	4	71–72	..	..
	NBD	..	..	72–73	..	..
1,2-Dibromo-1,3-diphenylpropane[f]	Br_2	..	..	108–109	..	..
	NBA	..	..	106–108	..	..
	NBD	..	..	106–108	..	..
1,2-Dibromo-2-methylpropane[g]	NBA	37–38	9	..	1.545	1.4800
		145–146	745	..	1.528	1.4800
Ethyl 1,2-dibromohydrocinnamate[h]	NBA	..	..	73–74	..	..
Methyl 1,2-dibromohydrocinnamate[h]	NBA	..	..	115–116	..	..
trans-α,α'-Dibromostilbene[g]	NBA	..	..	208–209	..	..
meso-α,α'-Dibromobibenzyl[g]	NBA	..	..	243–244	..	..
2,3-Dibromo-3-phenylpropiophenone[13]	NBA	..	..	158–159	..	..
α,β-Dibromostyrene[i]	NBA	101–104	4	..	..	..

[a] All m.p.'s corrected. Mixtures of solid bromination products with authentic samples gave no lowered m.p.'s. [b] Lit. b.p. 99–100° (27 mm.), n_D^{22} 1.5001 [Hurd and Bennett, *J. Am. Chem. Soc.*, **51**, 3675 (1929)]. [c] *Anal.* Calc'd for $C_7H_{12}Br_2$: Br, 60.2%. Found: Br, 58.8%. The product slowly decolorized bromine in carbon tetrachloride and potassium permanganate in acetone. Sodium iodide in acetone gave an immediate white precipitate with some light brown color. [d] Lit. b.p. 97–98° (10 mm.), d_4^{16} 1.7898, n_D^{16} 1.5540 [Coffey, *Rec. trav. chim.*, **42**, 398 (1923)]. [e] Lit. b.p. 69–72° (13 mm.), n_D^{20} 1.5285.[17] [f] Lit. m.p. 112° (block) when prepared from the oily olefin of unknown configuration.[29] [g] Lit. b.p. 54–56° (24 mm.), 149–151° (760 mm.), n_D^{20} 1.5119, d_4^{20} 1.7827 [Krestinsky, *Ber.*, **55**, 2754 (1922)]. Distillation at atmospheric pressure gave rise to fumes of hydrogen bromide and a distillate which decolorized bromine in carbon tetrachloride and potassium permanganate in acetone. [h] Lit. m.p. 117° [Anschütz and Kinnicutt, *Ber.*, **11**, 1214 (1878)]. [i] Lit. b.p. 132–135° (15 mm.) [Nef, *Ann.*, **308**, 273 (1898)].

and kept at 75°. On the day before a bromination was to be carried out 10.2 g. (0.05 mole) of the finely divided diacetimidomagnesium bromide was placed in an all glass vessel in contact with excess bromine vapor and left overnight. The excess bromine was then pumped off and the residue was extracted with two 25 ml. portions of warm chloroform. The orange solution was used in the bromination experiments.

The attempted synthesis of *N*-bromodiacetimide by means of the usual basic brominations which were used in the synthesis of *N*-bromoacetamide and *N*-bromosuccinimide gave no isolable product. The method[26] of bromination of the silver salt of diacetimide in trifluoroacetic acid likewise gave no isolable product.

2-Methyl-2-hexene. This compound was prepared by the condensation of n-butylmagnesium bromide with acetone followed by dehydration of the carbinol formed.[27]

1,3-Diphenyl-1-propanol. A solution of 100 g. (0.48 mole) of benzalacetophenone in 400 ml. of 95% ethyl alcohol was hydrogenated over copper chromite at 1500 lb. per sq. inch and 140°. Distillation of the pale green solution yielded 83 g. (81%) of 1,3-diphenyl-1-propanol, b.p. 150–152° (2

(26) Henne and Zimmer, *J. Am. Chem. Soc.*, **73**, 1103 (1951).

(27) Edgar, Calingaert, and Marker, *J. Am. Chem. Soc.*, **51**, 1483 (1929).

mm.), d_4^{20} 1.0594, n_D^{20} 1.5734 which check well with reported[28] values.

1,3-Diphenylpropene. A mixture of 106 g. (0.50 mole) of 1,3-diphenyl-1-propanol and 45 ml. of 85% phosphoric acid was slowly distilled to yield 80 g. (85%) of 1,3-diphenylpropene, b.p. 144–145° (5 mm.) which was probably the product, b.p. 164–168° (11 mm.), of questionable geometric configuration often obtained in the synthesis of this olefin.[28,29]

Other olefins. Styrene was used without purification with the *tert*-butylcatechol stabilizer present. Cyclohexene was distilled from sodium wire and kept over sodium wire. All of the other olefins were either commercial products or were synthesized by methods appearing in the *Organic Syntheses* series.

Solvents. Chloroform was washed several times with concentrated sulfuric acid and then with water. It was dried over anhydrous potassium carbonate and then distilled. Carbon tetrachloride was distilled from phosphorus pentoxide. Commercial, thiophene-free benzene was used without change.

Bromination Experiments. In general, 0.1 mole of brominating agent was used in 50 to 150 ml. of solvent with varying amounts of olefin. In all of the reactions the *N*-bromoamide was the yield-limiting material. Conditions during the reaction were adjusted to suit the reactivity of the *N*-bromoamide. In general, the *N*-bromoacetamide reactions had to be controlled much more carefully, by adding one of the reagents a little at a time, than did those with *N*-bromosuccinimide. The general results of the brominations are summarized in Table I. The properties of the products are given in Table II. In general, good yields of succinimide were obtained from those reactions from which no *N*-bromosuccinimide could be recovered. Varying amounts of acetamide could be obtained from the reactions involving *N*-bromoacetamide. As much as a 55% was isolated when cooled in an ice-salt bath and as much as 65% was isolated when ether was present.

About 44 experiments of this type were carried out between styrene and *N*-bromoacetamide in order to try to isolate products more completely. In each case 0.1 mole of *N*-bromoacetamide in the solvent was heated to reflux and 0.05 mole of styrene was added as rapidly as the violence of the reaction would permit. The acetamide was precipitated by anhydrous hydrogen chloride to give bisacetamide hydrochloride, m.p. around 131°, in yields of 95–97% in the most quantitative experiments. Attempts to purify the oily residue by crystallization or distillation were usually terminated by the formation of a brittle resinous glass. Oxidation of 10 g. of the residue with hot basic permanganate in one experiment yielded 0.5 g. of benzoic acid as well as the resinous glass.

When such a reaction was carried out in carbon tetrachloride with 0.05 mole of stilbene present a 15% yield of stilbene dibromide and a 34% yield of styrene dibromide were obtained. A 55% yield of stilbene was recovered. With 0.025 mole of triphenylmethane and 0.025 mole of *N*-bromoacetamide with 0.125 mole of styrene in carbon tetrachloride, a 42% yield of styrene dibromide was isolated and 91% of the triphenylmethane was recovered.

One experiment was carried out in carbon tetrachloride on a carefully weighed sample of *N*-bromoacetamide. The reaction mixture was extracted with water. The water layer was divided into portions and shown to contain 74.5% of the nitrogen by Kjehldal analysis and 18.6% of the bromine by silver nitrate precipitation. The carbon tetrachloride solution was evaporated. The residue was shown to contain 21.7% of the nitrogen by Kjehldal analysis and 81.7% of the bromine by hot alcoholic silver nitrate precipitation.

A very careful experiment was carried out with 4.1 g. (0.023 mole) of tolan and 6.3 g. (0.046 mole) of *N*-bromoacetamide in 100 ml. of refluxing carbon tetrachloride. At the end of 20 hr. no more *N*-bromoacetamide was present. From the reaction mixture were obtained 2.5 g. (32%) of crude tolane dibromide and 2.5 g. (70%) of bisacetamide hydrochloride by the general methods described above.

In several cases reactions of the olefins with bromine in carbon tetrachloride were carried out for the purpose of preparing authentic samples of dibromides. The properties of these samples are included in Table II.

Bisacetamide hydrochloride. A solution of 4.0 g. (0.067 mole) of acetamide in 50 ml. of anhydrous chloroform was saturated with anhydrous hydrogen chloride to give 5.4 g. (104%) of bisacetamide hydrochloride, m.p. 128–129°. Crystallization from acetonitrile yielded 5.0 (96%) of the hydrochloride, m.p. 130–131°.

Anal. Calc'd for $C_4H_{11}N_2O_2Cl$: C, 31.07; H, 7.17; N, 18.12; Cl, 22.93. Neutralization equivalent weight, 155.9. Found: C, 31.12; H, 7.15; N, 17.67; Cl, 23.01. Neutralization equivalent weight, 154.6.

Bisacetamide hydrochloride has been reported,[25,30] to have a m.p. varying from 125–135°. It has also been reported[25,31] to be considerably more stable than the 1:1 salt which decomposed with loss of hydrogen chloride to give bisacetamide hydrochloride. No 1:1 salt was ever isolated in the present investigation, but analysis of some samples of bisacetamide hydrochloride of m.p. around 125° showed that they were probably contaminated with this salt. Recrystallization of such samples always gave bisacetamide hydrochloride of m.p. around 131°.

(28) Pfeiffer, Kalckbrenner, Kunze, and Levin, *J. prakt. Chem.*, [2] **119**, 109 (1928).

(29) Ramart and Arnagat, *Ann. chim.* [10] **8**, 310 (1927).

(30) Pinner and Klein, *Ber.*, **10**, 1896 (1877).

(31) Strecker, *Ann.*, **103**, 322 (1857).