196. *Some Observations on the Course of the Reaction between Ethylenic Compounds and* N-*Bromosuccinimide.*

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The reaction between *N*-halogenoimides and ethylenic compounds appears to involve two competing processes, leading to allylic substitution and halogen addition, respectively. Normally, substitution is predominant (Ziegler), but certain structural features promote addition which becomes the main reaction in the case of *cyclo*butene (Howton). Addition can also be promoted by certain catalysts; thus, whereas the action of *N*-bromosuccinimide on *cyclo*hexene ordinarily gives 3-bromo*cyclo*hexene, in the presence of alkylammonium salts 1 : 2-dibromo*cyclo*hexane is the major product. It is suggested that whereas substitution involves homolytic fission of the N–Br bond (Bloomfield), addition involves heterolytic fission which can be aided by complex formation with the *N*-halogenoimide. Addition compounds of *N*-bromosuccinimide and tetra-alkylammonium halides have been isolated.

The action of *N*-bromosuccinimide on allylbenzene results mainly in substitution, accompanied by allylic rearrangement, to give cinnamyl bromide. In the presence of triethylamine, however, which is rapidly converted into triethylamine hydrobromide, mainly 1 : 2-dibromo-3-phenylpropane is obtained. The action of 2 : 4 : *N*-trichloroacetanilide, even in the absence of salts, gives a mixture of substitution and addition products.

The action of *N*-bromosuccinimide on allylhexyne results mainly in substitution, accompanied by rearrangement, to give 1-bromonon-2-en-4-yne.

It was first shown by Ziegler and his co-workers (*Annalen*, 1942, **551**, 80) that *N*-bromosuccinimide and *cyclo*hexene give mainly 3-bromo*cyclo*hexene and succinimide. Allylic bromination of this type has since become a widely employed preparative method (for an excellent summary, see Djerassi, *Chem. Reviews*, 1948, **43**, 271) and it is now generally accepted that it involves homolytic fission of the N–Br bond. The assumption of a free-radical mechanism is supported, *inter alia*, by the fact that allylic bromination is catalysed by peroxides (Karrer and Schmid, *Helv. Chim. Acta*, 1946, **29**, 525) and promoted by illumination (Meystre and Miescher, *ibid.*, 1945, **28**, 1497; 1946, **29**, 33). A detailed reaction scheme has been put forward (Bloomfield, *J.*, 1944, 114) which involves (i) homolytic fission into $(CH_2\cdot CO)_2N\cdot$ and $Br\cdot$, (ii) abstraction of a hydrogen atom from the allyl position of the olefin by $(CH_2\cdot CO)_2N\cdot$, and (iii) reaction between the resulting allyl radical and bromosuccinimide to give the allylic bromide and $(CH_2\cdot CO)_2N\cdot$, followed again by (ii) in a chain process.

Reaction between N-*Bromosuccinimide and* cyclo*Hexene.*—In connection with other work, a closer study has been made of the products of the reaction between *N*-bromosuccinimide and *cyclo*hexene (cf. Braude and Waight, *Nature*, 1949, **164**, 241). Using excess of *cyclo*hexene and carbon tetrachloride as a diluent, Ziegler and his co-workers (*loc. cit.*) obtained almost theoretical yields (based on the bromo-imide) of succinimide, and 80—90% yields of 3-bromo*cyclo*hexene, together with small amounts of undistilled residues. More recently, Howton (*J. Amer. Chem. Soc.*, 1947, **69**, 2060) carried out the reaction in benzene and isolated, besides 3-bromo*cyclo*hexene (50%), 1 : 2-dibromo*cyclo*hexane (15%) and small quantities of 3 : 6-dibromo*cyclo*hexene and *N*-phenylsuccinimide. We find that appreciable proportions of 1 : 2-dibromo*cyclo*hexane are also formed in light petroleum or chloroform; moreover, the yields of 3-bromo*cyclo*hexene are markedly lower, and those of the saturated dibromide are higher, on addition of alkylammonium salts and, to a smaller extent, of inorganic salts (see Table). The same effect can be produced by the addition of triethylamine; separate experiments showed that triethylamine rapidly reacted with *N*-bromosuccinimide to give succinimide and triethylamine hydrobromide. It will be noted that, unlike the substitution reaction (*S*), the addition reaction (*A*) requires the provision of two extra hydrogen atoms which are presumably derived either from part of the *cyclo*hexene or from the solvent.

$$(S) \quad C_6H_{10} + (CH_2{\cdot}CO)_2NBr \longrightarrow C_6H_9Br + (CH_2{\cdot}CO)_2NH$$

$$(A) \quad C_6H_{10} + 2(CH_2{\cdot}CO)_2NBr \xrightarrow{2H} C_6H_{10}Br_2 + 2(CH_2{\cdot}CO)_2NH$$

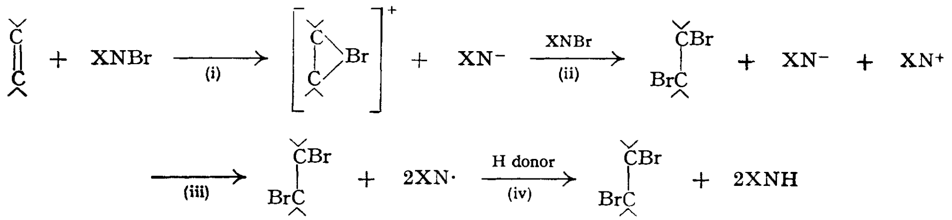
Bromination of cyclo*hexene with* N-*bromosuccinimide in chloroform.*

Catalyst	Mol. propn.*	Yield (%) * of 3-bromo*cyclo*hexene	 1 : 2-dibromo*cyclo*hexane
—	—	30	12
LiCl	0·5	30	20
KCl	0·25	31	31
NEt_3	0·1	18	36
NEt_3,HBr	0·2	4	50
NEt_4Br	0·4	2	74
NEt_4I	0·4	3	62

* Based on *N*-bromosuccinimide.

The formation of saturated dibromo-derivatives, sometimes as major products, has also been observed in several other cases, *e.g.*, in the reaction between *N*-bromosuccinimide and 3-β-acetoxy-24 : 24-diphenyl*allo*chol-23-ene (Wieland and Miescher, *Helv. Chim. Acta*, 1947, **30**, 1876), *cyclo*butene and methylene*cyclo*butane (Buchmann and Howton, *J. Amer. Chem. Soc.*, 1948, **70**, 2517, 3510), ethyl tetrolate (English and Gregory, *ibid.*, 1949, **71**, 1115), methyl and phenyl styryl ketone (Southwick, Pursglove, and Numerof, *ibid.*, 1950, **72**, 1600), and allyl cyanide (Waight, Thesis, London, 1950), between *N*-bromophthalimide and *cyclo*hexene (Ziegler *et al.*, *loc. cit.*), and between *N*-bromoacetamide and stilbene (Buckles, *J. Amer. Chem. Soc.*, 1949, **71**, 1157). It thus appears that the addition reaction generally competes to some extent with the more usual substitution reaction and that the balance between the two reactions depends (*a*) on the structure of the *N*-halogeno-compound, (*b*) on the structure of the olefin, (*c*) on the solvent and experimental conditions, and (*d*) on the presence of certain catalysts, such as alkylammonium salts, which promote the addition reaction.

It was suggested by Wieland and Miescher (*loc. cit.*) that the addition reaction is due to free bromine, liberated by the interaction of *N*-bromosuccinimide and hydrogen bromide formed by side reactions such as dehydrohalogenation of the allylic bromide. No hydrogen bromide or bromine are observed, however, in the reactions described above. 3-Bromo*cyclo*hexene is recovered largely unchanged after treatment with tetraethylammonium bromide in boiling chloroform, and no easily detectable amount of bromine is liberated in a boiling solution of *N*-bromosuccinimide and triethylamine hydrobromide in chloroform. Further convincing evidence against the intervention of free bromine has been adduced by Southwick *et al.* (*loc. cit.*) and there can be no doubt that the addition reaction involves the direct interaction between the *N*-halogeno-compound and the olefin. In some of the cases reported by Buckles and by Southwick, the addition reactions are accelerated by peroxides and light and appear to be radical reactions, like allylic substitution. The salt-catalysed nature of the bromine-addition reactions of *N*-bromosuccinimide with *cyclo*hexene and also with allylbenzene (see below), however, suggests the possibility that they may involve *heterolytic* rather than homolytic fission of the N–Br bond as the primary and rate-determining step, although the formation of succinimide undoubtedly involves a subsequent homolytic hydrogen abstraction. A similar conclusion was reached by Buckles (*loc. cit.*) who found that, whereas the peroxide-catalysed reaction of *cis*-stilbene with *N*-bromoacetamide yielded *meso*stilbene dibromide, in the presence of hydrogen bromide the product was racemic stilbene dibromide. That the homolytic and the heterolytic mode of fission take place with comparable ease is indicated by the ionic reactions which *N*-halogeno-compounds undergo in polar solvents (cf. Winstein and Lucas, *J. Amer. Chem. Soc.*, 1939, **61**, 1576; Raphael, *J.*, 1949, S 44) and is understandable in view of the low bond energy (*ca.* 33 kcal./mole) and very similar electronegativities (3·0 and 2·8; Pauling, "The Nature of the Chemical Bond," New York, 1940) of nitrogen and bromine. A plausible mechanism for the addition reaction is as follows:



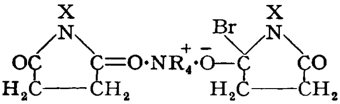
[$X = (CH_2{\cdot}CO)_2$.]

The first step is the slow reaction with the olefin to give the bromonium ion and a succinimide anion. Reaction (ii) gives the dibromo-compound and a succinimide cation. The two succinimide ions then undergo electron-transfer and are converted into two succinimidyl radicals; finally, each radical abstracts a hydrogen atom from a donor. The first step is entirely analogous to that generally accepted for the addition of bromine itself to olefins (cf. Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947; De La Mare, *Quart. Reviews*, 1949, **3**, 126). As would be expected from step (ii), the 1 : 2-dibromo*cyclo*hexane formed appears to be the *trans*-isomer, identical in physical properties with that obtained by the addition of bromine itself to *cyclo*hexene (Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2792). The fact that the addition is completed by reaction with a second molecule of bromo-imide rather than by the formation of the 1-bromo-2-succinimido-derivative is comprehensible in terms of the relative strengths of the C–N, C–Br and N–Br bonds and by analogy with ordinary addition, which frequently involves concerted attack by two or more molecules of halogen (cf. De La Mare, *loc. cit.*; De La Mare and Robertson, *J.*, 1950, 2838). It is of interest in this connection, however, that 1-bromo-2-phthalimido*cyclo*hexane is obtained as a by-product in the reaction between *N*-bromophthalimide and *cyclo*hexene (Ziegler *et al.*, *loc. cit.*). Step (iii) might perhaps be expected to yield the unknown disuccinimidyl XN·NX, but attempts to prepare this compound by the reaction of *N*-bromosuccinimide with silver succinimide or mercury were unsuccessful (see Experimental) and this compound is evidently very unstable, probably dissociating with ease into two succinimidyl radicals. Thus, step (iii) in the above scheme is a reasonable hypothesis. Step (iv) is entirely analogous to the hydrogen abstraction involved in the substitution reaction (Bloomfield, *loc. cit.*). Although some of the intermediates above have been written as separate ions for clarity, steps (i) and (ii) may represent partial rather than complete electron-transfers and the bromonium and succinimide ions undoubtedly remain in their mutual spheres of influence until step (iii) is complete. This is also indicated by the fact that no iodine-containing products are obtained when the reaction is carried out in the presence of tetraethylammonium iodide.

The two modes of reaction of *N*-bromosuccinimide with olefins are paralleled by two corresponding modes of reaction with aromatic compounds. Thus, it has been shown by Schmid (*Helv. Chim. Acta*, 1946, **29**, 1144) that toluene reacts with *N*-bromosuccinimide in the presence of benzoyl peroxide to give benzyl bromide, whereas in the presence of aluminium trichloride and similar catalysts a mixture of bromotoluenes is formed. Side-chain bromination is, of course, analogous to allylic substitution, while nuclear bromination is analogous to olefin addition (cf. Braude, *Ann. Reports*, 1949, **46**, 138) and almost certainly proceeds by an ionic mechanism. Attempts to investigate the effects of aluminium trichloride on the reaction between *cyclo*hexene and *N*-bromosuccinimide were unsuccessful because of the explosive nature of the reaction mixture.

The influence of the structure of the olefin and of the *N*-halogeno-compounds fits in with the idea of competing homolytic substitution and heterolytic addition reactions. Addition is favoured by olefinic compounds in which the ethylenic system is either relatively unstable thermodynamically, as in *cyclo*butene, or highly polarised, as in phenyl styryl ketone. Similarly, addition is more pronounced with those *N*-halogeno-compounds which are less reactive in allylic substitution, *i.e.*, in which the *N*–halogen bond is more polar.

The question arises as to the mode of functioning of alkylammonium salts in promoting the addition reaction. Several ways can be envisaged, *e.g.*, (*a*) inhibition of the radical reaction by chain-breaking or (*b*) facilitation of the heterolytic fission of the N–Br bond, either (i) indirectly by the increase in the ionising properties of the solvent, or directly by association with (ii) the *N*-halogeno-compound or (iii) the olefin. The first way seems the least likely, *inter alia*, because tetraethylammonium bromide is more effective than triethylamine hydrobromide which might be expected to be the better radical-chain inhibitor. Amongst the other possibilities, (*b*, i) alone also seems improbable since the alkylammonium salts will exist largely as undissociated ion-pairs in the organic solvents, while the inorganic salts are practically insoluble, so that the change in ionic strength will be small. Association between alkylammonium cations and the olefin may take place, analogous to the π-complex formation observed with many other cations (cf. Winstein and Lucas, *J. Amer. Chem. Soc.*, 1938, **60**, 836; Dewar, *J.*, 1946, 406); this would, however, facilitate nucleophilic rather than electrophilic attack, and (*b*, ii) would therefore require a reversal of the sequence of steps (i) and (ii) in the reaction scheme above. The most likely explanation appears to be (*b*, iii); association between *N*-bromosuccinimide and tetraethylammonium bromide and iodide almost certainly occurs since unstable addition compounds, as well as a more stable adduct with succinimide, can be isolated. The nature of the addition compounds has not been elucidated, but any interaction of this kind will undoubtedly increase the ionic character of the N–Br bond and facilitate steps (i) and (ii) in the addition reaction. The adducts all contain two molecules of imide and one molecule of tetra-alkylammonium salt, and a possible formulation is that shown below in which the carbonyl group of one imide molecule acts as a base and the carbonyl group of the other as an acid:



Reaction between N-*Halogenoimides and Allylbenzene.*—Several instances have been described of allylic rearrangement accompanying the reactions of *N*-bromosuccinimide with ethylenic compounds (*inter alia*, Djerassi, *loc. cit.*; Karrer and his co-workers, *Helv. Chim. Acta*, 1947, **30**, 863, 1771; 1948, **31**, 395; Bateman, Cunneen, Fabian, and Koch, *J.*, 1950, 936; Bateman and Cunneen, *ibid.*, p. 941; Gensler, *J. Amer. Chem. Soc.*, 1951, **73**, 1071; Barnes and Buckwalter, *ibid.*, p. 3858). The occurrence of rearrangement is compatible with the generally accepted view that such reactions involve the intervention of allylic radicals, since the latter will be subject to electron-resonance and will give rise to mixtures of products depending on the relative contributions of structures such as $X{\cdot}\dot{C}H{\cdot}CH{:}CHY$ and $X{\cdot}CH{:}CH{\cdot}\dot{C}HY$ to the hybrid radical. As has been pointed out by Bateman *et al.* (*loc. cit.*), however, the production of isomeric bromides is often to be expected quite independently of their mode of formation, since allylic bromides are known to undergo isomerisation with ease, most probably by a homolytic mechanism (for references see Braude, *Ann. Reports*, 1949, **46**, 129; *Quart. Reviews*, 1950, **4**, 404).

Most of the cases in which rearrangement accompanying halogenation has so far been observed relate to derivatives containing only alkyl substituents directly attached to the allyl grouping; in such circumstances the difference in energy content of the two isomers is relatively small and the equilibrium mixture contains isolatable proportions of both bromides at ordinary temperatures. In allyl derivatives containing an unsaturated substituent, on the other hand, the equilibrium will be far on one side owing to the extra resonance energy associated with a conjugated system and it would therefore be expected that the halogenation of compounds such as allylbenzene (I) will be accompanied by almost complete rearrangement. Since 1-phenylallyl bromide and similar bromides are unknown, it appeared desirable to confirm this expectation, particularly in view of the fact that certain other reactions believed to involve phenylallyl radicals have been reported to furnish mixtures containing as much as 25% of the unconjugated 1-phenylallyl derivatives (Kharasch, Lambert, and Urry, *J. Org. Chem.*, 1945, **10**, 298; Koch, *J.*, 1948, 1111).

The reaction of *N*-bromosuccinimide with allylbenzene, like that with propenylbenzene (Ziegler *et al.*, *loc. cit.*), proceeds very slowly in dilute carbon tetrachloride solution, but is greatly accelerated by benzoyl peroxide. The main product (50%) is cinnamyl bromide (II), identified by its melting point and ultra-violet light-absorption ($\lambda_{max.}$ 2590 Å, ε 17000).

$$\underset{\text{(IV)}}{\text{Ph}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}} \longleftarrow \underset{\text{(I)}}{\text{Ph}\cdot\text{CH}_2\cdot\text{CH:CH}_2} \longrightarrow \underset{\text{(II)}}{\text{Ph}\cdot\text{CH:CH}\cdot\text{CH}_2\text{Br}} \longrightarrow \underset{\text{(III)}}{\text{Ph}\cdot\text{CHBr}\cdot\text{CH:CH}_2}$$

1-Phenylallyl bromide (III) would only exhibit low-intensity absorption in this region and it can be estimated from the spectral data for the crude distillable products that less than 10% of unconjugated bromide was present, if any. Since the preliminary report of this work (*Nature*, 1949, **164**, 241) a similar conclusion has been reached by Lora-Tamayo, Martin-Panzio, and Perez Ossorio (*J.*, 1950, 1418), though on rather less secure evidence.

Similar results are obtained when the reaction is carried out in light petroleum (b.p. 80—100°) either in the presence of benzoyl peroxide or on irradiation with ultra-violet light. The course of the bromination is completely altered, however, on the addition of catalytic quantities of triethylamine, which is rapidly converted into triethylamine hydrobromide by *N*-bromosuccinimide (see above) Under these conditions, the main product is, not cinnamyl bromide, but 1 : 2-dibromo-3-phenylpropane (IV), analogously to the "salt-catalysed" formation of dibromo*cyclo*hexane from *cyclo*hexene and *N*-bromosuccinimide.

Unlike allyl bromides, allyl chlorides do not readily isomerise (cf. Braude, *loc. cit.*). In order to test whether the extent of rearrangement in the halogenation of allylbenzene is dependent on the entering halogen radical, the reaction of the hydrocarbon with 2 : 4 : *N*-trichloroacetanilide (cf. Ziegler *et al.*, *loc. cit.*) was examined. Under the conditions employed for the bromination, this yields very slowly a mixture of cinnamyl chloride and 1 : 2-dichloro-3-phenylpropane. The two products are not readily separable by fractionation on a small scale, but the analytical data indicate that the proportion of any 1-phenylallyl chloride present amounted to less than 10%.

Reaction between N-*Bromosuccinimide and Allylhexyne.*—As a further example, the bromination of allylhexyne (non-1-en-4-yne) (V) with *N*-bromosuccinimide has been carried out. This is much slower than that of allylbenzene: even in the presence of benzoyl peroxide, a large proportion of the hydrocarbon is recovered unchanged after 20 hours in boiling carbon tetrachloride. As in the previous case, the substitution reaction is

$$\text{(V)}\ \text{Bu}^{\text{n}}\cdot\text{C}\vdots\text{C}\cdot\text{CH}_2\cdot\text{CH:CH}_2 \qquad\qquad \text{Bu}^{\text{n}}\cdot\text{C}\vdots\text{C}\cdot\text{CH:CH}\cdot\text{CH}_2\text{Br}\ \text{(VI)}$$

accompanied by extensive, though not necessarily complete, isomerisation. The main product isolated is the primary bromide (VI), which exhibits ultra-violet light absorption properties typical of a conjugated vinylacetylene and was converted, by alkaline hydrolysis and catalytic hydrogenation, into nonyl alcohol, identified as the 3 : 5-dinitrobenzoate. The only other recorded example of the halogenation of an acetylenic derivative with *N*-bromosuccinimide appears to be that of ethyl tetrolate which undergoes addition to give ethyl αβ-dibromocrotonate rather than allylic substitution (English and Gregory, *J. Amer. Chem. Soc.*, 1949, **71**, 1115).

EXPERIMENTAL

Bromination of cyclo*Hexene.*—*N*-Bromosuccinimide (crystallised from boiling water and vacuum-dried) was added to the solvent containing the catalyst (if any) and, after any ensuing reaction was complete, *cyclo*hexene was added. The mixture was then heated under reflux for 20—60 minutes, cooled, and filtered. The residue (A) was extracted with more solvent, and the combined filtrate and washings were concentrated by distillation and then diluted with carbon tetrachloride, if necessary, to precipitate more succinimide and alkylammonium salts which were filtered off (B). The remaining solution was fractionated under reduced pressure, and the proportions of 3-bromo*cyclo*hexene (n_D^{20} 1·5270) and 1 : 2-dibromo*cyclo*hexane (n_D^{20} 1·5516) were estimated by refractive-index measurements. In some cases, the two bromo-compounds were also separated by treatment with triethylamine, 3-bromo*cyclo*hexene giving a quaternary salt, m. p. 197° (cf. Howton, *loc. cit.*). The residues (A) and (B) were combined and succinimide was isolated from them by extraction with acetone or benzene–ethanol. Three typical experiments are recorded below.

(*a*) A mixture of *N*-bromosuccinimide (22 g.), potassium chloride (3·5 g.), *cyclo*hexene (10 g.), and chloroform (50 ml.) was heated under reflux for 1 hour. Working up as described gave succinimide, m. p. 123° (18 g., 90%), and a mixture of bromination products which was separated into fractions: (i) b. p. 76—90°/14 mm., n_D^{20} 1·5255 (3·3 g.), (ii) b. p. 90—96°/14 mm., n_D^{20} 1·5379 (5·7 g.), and (iii) b. p. 96—102°/14 mm., n_D^{20} 1·5425 (8·4 g.); this represents a total yield of 9·9 g. (31%) of 3-bromo*cyclo*hexene and 7·5 g. (31%) of 1 : 2-dibromo*cyclo*hexane.

(*b*) A mixture of *N*-bromosuccinimide (25 g.), tetraethylammonium bromide (13 g.), *cyclo*hexene (16 g.), and chloroform (70 ml.) was heated under reflux for 20 minutes. Working up as above gave fractions: (i) b. p. 102—106°/18 mm., n_D^{20} 1·5450 (1·8 g.), (ii) b. p. 106—107°/18 mm., n_D^{20} 1·5502 (6 g.), and (iii) b. p. 107—109°/18 mm., n_D^{20} 1·5510 (5 g.) (Found: Br, 65·6. Calc. for $C_6H_{10}Br_2$: Br, 66·1%), representing a total yield of 0·5 g. (2%) of 3-bromo*cyclo*hexene and 12·3 g. (74%) of dibromo*cyclo*hexane. The solid products contained succinimide and an addition *compound* of the latter with tetraethylammonium bromide which separated from ethanol in orange crystals, m. p. 170—171° (Found: C, 47·4; H, 7·6; N, 9·9; Br, 19·9. $2C_4H_5O_2N,C_8H_{20}NBr$ requires C, 47·1; H, 7·4; N, 10·3; Br, 19·6%).

(*c*) A mixture of *N*-bromosuccinimide (25 g.), tetraethylammonium iodide (15·5 g.), *cyclo*hexene (16 g.), and chloroform (100 ml.) was heated under reflux for 40 minutes. Working up as above gave fractions: (i) b. p. 44—45°/0·1 mm., n_D^{20} 1·5490 (6 g.), and (ii) b. p. 46—50°/0·1 mm., n_D^{20} 1·5506 (4·6 g.), representing a total yield of 0·6 g. (3%) of 3-bromo*cyclo*hexene and 10 g. (62%) of 1 : 2-dibromo*cyclo*hexane. Both fractions gave negative tests for iodine.

Bromination of Allylbenzene.—(*a*) A mixture of *N*-bromosuccinimide (20 g.), allylbenzene (13 g.), and carbon tetrachloride (130 ml.) was refluxed for 2 hours. Little reaction occurred and benzoyl peroxide (500 mg.) was added. After a further 2 hours' heating, the mixture was cooled and filtered. The residue consisted mainly of succinimide, m.p. 124° after crystallisation from methanol. The solution was distilled under reduced pressure. The fractions with b. p. 70—85°/0·05 mm., n_D^{20} 1·6100–6130, $\lambda_{max.}$ 2590 Å, $E_{1\,cm.}^{1\%}$ 730—830, were dissolved in pentane; on cooling, cinnamyl bromide (11 g., 50%), m. p. 28—30°, separated. Two further crystallisations raised the m.p. to 30°, undepressed on admixture with an authentic specimen prepared by the reaction of cinnamyl alcohol with phosphorus tribromide. The pure bromide had $\lambda_{max.}$ 2590 ($E_{1\,cm.}^{1\%}$ 850) and 2640 Å ($E_{1\,cm.}^{1\%}$ 820) in hexane.

(*b*) A mixture of *N*-bromosuccinimide (9 g.), allylbenzene (12 g.), and light petroleum (b. p. 80—100°; 100 ml.) was heated under reflux in a "Pyrex" flask irradiated with a mercury arc. Distillation afforded cinnamyl bromide (7 g., 70% based on *N*-bromosuccinimide), b. p. 51—52°/0·005 mm., n_D^{20} 1·6130—1·6150, m. p. 30° after one crystallisation from pentane.

(*c*) *N*-Bromosuccinimide (31 g.) was added portionwise to a solution of allylbenzene (21 g.) and triethylamine (1·7 g.) in light petroleum (b. p. 80—100°; 200 ml.). Benzoyl peroxide (500 mg.) was then added and the mixture was heated under reflux for 30 minutes. After filtration, most of the solvent was distilled off, N-acetic acid (100 ml.) was added, and the resulting solution was extracted with ether. Distillation of the extract through a short Fenske column afforded unchanged allylbenzene (10 g.), and dibromophenylpropane (10·6 g., 44% based on *N*-bromosuccinimide), b. p. 76—78°/0·05 mm., n_D^{20} 1·5860, $\lambda_{max.}$ 2590 ($E_{1\,cm.}^{1\%} = 28$) (Found: C, 39·6; H, 3·9; Br, 56·6. Calc. for $C_9H_{10}Br_2$: C, 38·9; H, 3·6; Br, 57·5%). An authentic sample, prepared by the addition of bromine to allylbenzene in carbon tetrachloride, had b. p. 78°/0·05 mm., n_D^{20} 1·5857.

Chlorination of Allylbenzene.—2 : 4 : *N*-Trichloroacetanilide was prepared by adding a solution of acetanilide in acetic acid to 15% aqueous sodium hypochlorite solution and, after crystallisation from chloroform–light petroleum, had m. p. 68—71°, not raised by further treatment with hypochlorite (Chattaway and Orton, *J.*, 1899, 1052, give m. p. 77°). A mixture of the chloro-amine (20 g.), allylbenzene (10 g.), carbon tetrachloride (100 ml.), and benzoyl peroxide (500 mg.) was heated under reflux for 60 hours. After cooling and filtering, the liquid products were distilled, giving unchanged allylbenzene (6 g.) and a mixture of chlorinated hydrocarbons (3 g.), b. p. 68—72°/0·6 mm., n_D^{21} 1·5686. Analytical data (total Cl, 26·8; Cl, hydrolysable by aqueous potassium carbonate, 16·0%; $\lambda_{\text{max.}}$ 2550 Å., $E^{1\%}_{1\,\text{cm.}}$ 1000. Calc. for cinnamyl chloride: Cl, 23·3%; $E^{1\%}_{1\,\text{cm.}}$ 1300) indicate that the latter consisted of cinnamyl chloride (*ca.* 70%) and 1 : 2-dichloro-3-phenylpropane (30%).

Bromination of Allylhexyne.—A mixture of *N*-bromosuccinimide (18 g.), allylhexyne (12·5 g.; Danehy, Killian, and Nieuwland, *J. Amer. Chem. Soc.*, **1936**, **58**, 611), carbon tetrachloride (50 ml.) and benzoyl peroxide (500 mg.) was heated under reflux for 10 hours. After cooling, the mixture was filtered and distilled, giving unchanged allylhexyne (8 g.) and 1-*bromonon*-2-*en*-4-*yne* (3 g.), b. p. 63—64°/0·4 mm., n_D^{21} 1·5145 (Found: Br, 40·3. $C_9H_{13}Br$ requires Br, 39·9%). Light absorption in hexane: $\lambda_{\text{max.}}$ 2420 and 2490 Å (ε 8000). The bromide was refluxed with sodium carbonate (1·5 g.) in aqueous acetone, and the resulting carbinol (1·5 g.), b. p. 84—88°/1·5 mm., $\lambda_{\text{max.}}$ 2280 Å (ε 12 000) was hydrogenated in methanol in the presence of a platinum catalyst, giving nonyl alcohol, b. p. 98°/8 mm., n_D^{20} 1·4301, which was identified as the 3 : 5-dinitrobenzoate, m. p. 52—53° (from methanol), undepressed on admixture with an authentic specimen. The latter was obtained from a sample of nonyl alcohol (2·5 g., 55%) prepared by treating pelargonic acid (5 g.) with lithium aluminium hydride (2·5 g.) in ether at room temperature.

Reaction between N-*Bromosuccinimide and Triethylamine.*—*N*-Bromosuccinimide (6 g.) was added portionwise to a solution of triethylamine (7 g.) in carbon tetrachloride (20 ml.) at 0°. The crystalline solid which separated was filtered off and extracted with acetone. The residue was triethylamine hydrobromide (3 g.), m. p. 245—246°, undepressed on admixture with an authentic sample. The acetone solution was evaporated to dryness, giving succinimide (2·5 g.) which was crystallised from ethanol–light petroleum and had m. p. 123°, undepressed on admixture with an authentic specimen. The reaction between *N*-bromosuccinimide and triethylamine has previously been investigated by Cosgrove and Waters (*J.*, 1949, 907) who reported only the formation of succinimide together with traces of other materials, but the method of working up employed by these authors would have precluded the isolation of triethylamine hydrobromide.

Reaction between N-*Bromosuccinimide and Tetraethylammonium Halides.*—*N*-Bromosuccinimide (0·71 g.) and tetraethylammonium bromide (0·42 g.) were dissolved in hot chloroform (50 ml.). The solvent was evaporated and the resulting *adduct* was recrystallised several times from chloroform, giving fine, colourless crystals, m. p. 144° (Found: C, 33·8; H, 5·2; N, 7·4; Br, 42·8. $2C_4H_4O_2NBr,C_8H_{20}NBr$ requires C, 33·9; H, 4·95; N, 7·4; Br, 42·4%). The adduct is soluble in benzene and can be recovered unchanged. It is also soluble in water, and the aqueous solution gives a positive test for bromide anion but fails to liberate iodine from acidified potassium iodide solution (cf. *N*-bromosuccinimide).

A solution of *N*-bromosuccinimide (0·71 g.) and tetraethylammonium iodide (0·51 g.) in hot chloroform (50 ml.) on cooling deposited orange crystals of an adduct from which no succinimide could be extracted with benzene. Recrystallisation from chloroform or chloroform–benzene was attended by partial decomposition and gave pale orange crystals, m. p. 115—116° (Found: C, 30·6; H, 4·4; N, 6·15. $2C_4H_4O_2NBr,C_8H_{20}NI$ requires C, 31·3; H, 4·6; N, 6·85%).

Attempts to prepare Disuccinimidyl.—(*a*) Silver succinimide (6 g.), prepared by treating succinimide with aqueous ethanolic silver nitrate, was added to a suspension of *N*-bromosuccinimide (7 g.) in benzene (100 ml.). Mixing caused the solution to become red, and a neutral gas was evolved. The mixture was mechanically shaken in a stoppered flask for 20 hours and filtered. The residue was silver bromide (6·3 g., 100%). The solution on evaporation yielded a small quantity of succinimide and an intractable tar.

(*b*) From a similar experiment in which mercury was substituted for silver succinimide, the only product isolated was mercury succinimide which crystallised from boiling ethanol and had m. p. 336° [Found: N, 7·07. Calc. for $(C_4H_4O_2N)_2Hg$: N, 7·05%].

We thank the Department of Scientific and Industrial Research for a maintenance grant (to E. S. W.).

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[*Received, November 2nd*, 1951.]