Liberation of the enclosed component on solution of the substance is typical behaviour for the compounds 3 quinol. M^2 .

An X-ray examination of the crystals showed that they have the β -type structure common to this series of molecular compounds³.

A detailed crystal structure examination is being made.

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¹ Powell, H. M., *J. Chem. Soc.*, 61 (1948).

² Palin, D. E., and Powell, H. M., *J. Chem. Soc.*, 208 (1947).

³ Palin, D. E., and Powell, H. M., *J. Chem. Soc.*, 815 (1948).

N-Bromosuccinimide as a Reagent for Bromine Addition

It was first shown by Ziegler and co-workers¹ that *N*-bromosuccinimide (XNBr) reacts with cyclohexene to give 3-bromocyclohexene (I) and succinimide. We have found that if the reaction is carried out in chloroform, benzene or petrol solution in the presence of salts such as tetraethylammonium bromide, tetraethylammonium iodide, or triethylamine hydrobromide, 1:2-dibromocyclohexane (II) is formed instead of 3-bromocyclohexene, in proportions depending on the exact conditions employed. The same effect can be brought about by the addition of small amounts (c. 10 mol. per cent based on *N*-bromosuccinimide) of triethylamine, which reacts with part of the *N*-bromosuccinimide to give triethylamine hydrobromide and succinimide.

Analogous observations were made with the reaction between *N*-bromosuccinimide and allylbenzene. In the absence of special catalysts, cinnamyl bromide (III) is formed by substitution in the allyl position, accompanied by rearrangement. In the presence of small amounts of triethylamine, 1-phenyl-2:3-dibromopropane (IV) is obtained instead.

Moreover, the salt-catalysed reaction resulting in bromine addition is relatively slow and not accelerated by benzoyl peroxide, whereas the normal reaction resulting in substitution is relatively fast and strongly accelerated by benzoyl peroxide. It will be noted that the addition reaction requires the provision of two extra hydrogen atoms. Since succinimide is always obtained in nearly quantitative yield, whereas the yield of isolatable bromination product is only of the order of 50 per cent, the extra hydrogen atoms must be derived either from the allylic reactant or from the solvent.

These investigations are not yet complete, but we are prompted to record our observations at this stage in view of some recent publications² in which it is reported that, even in the absence of special catalysts, the reaction between *N*-bromosuccinimide and cyclohexene affords a very small proportion, and the reaction with cyclobutene and methylenecyclobutane a large proportion, of the 1:2-dibromo derivatives.

Moreover, Buckles³ has recently shown that another *N*-halogen compound, *N*-bromoacetamide, reacts with ethylenic compounds in chloroform solution to give the dibromo derivatives. The formation of some 1:2-dibromocyclohexane in the reaction between *N*-bromophthalimide and cyclohexene was previously reported by Ziegler and co-workers¹. The addition reaction can thus be promoted by structural as well as external factors.

It is now generally accepted that allylic substitution with *N*-bromosuccinimide is a free radical chain reaction involving the homolytic fission of the N—Br bond⁴. The mechanism of the addition reaction must be different and is of interest. The fact that the addition reaction is catalysed by salts, and, unlike the substitution reaction, not accelerated by peroxides, together with certain other considerations, suggests that it may involve the heterolytic fission of the N—Br bond as the primary and rate-determining step; but the formation of succinimide almost certainly involves a subsequent homolytic hydrogen-abstraction. The following scheme is tentative:

This work is still in progress, and details will be published elsewhere in due course.

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¹ Ziegler, Späth, Schaaf, Schumann and Winkelmann, *Annalen*, **551**, 80 (1942).

² Howton, *J. Amer. Chem. Soc.*, **69**, 2060 (1947). Buchmann and Howton, *ibid.*, **70**, 2517, 3510 (1948).

³ Buckles, *J. Amer. Chem. Soc.*, **71**, 1157 (1949).

⁴ Bloomfield, *J. Chem. Soc.*, 114 (1944).