

UNUSUAL BROMINATIONS WITH N-BROMOPOLYMALEIMIDE

Carmela Yaroslavsky, Abraham Patchornik and
Ephraim Katchalski

Department of Biophysics, The Weizmann Institute of Science,
Rehovot, Israel

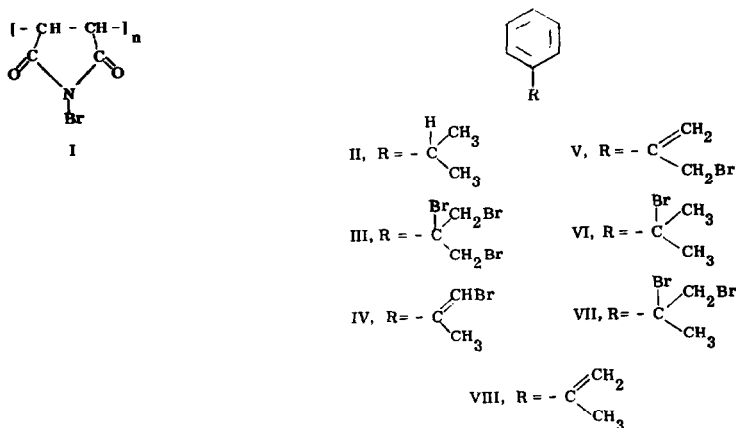
(Received in UK 13 July 1970; accepted for publication 5 August 1970)

We wish to report the formation of several unexpected products from the treatment of some benzylic and olefinic compounds with N-bromopolymaleimide (PNBS).

Polymaleimide¹ was prepared by free radical polymerization of maleimide, in the presence of 2.5 - 5% divinylbenzene. It was brominated by addition of bromine to a suspension of the polymer in aqueous sodium hydroxide solution. The average yield of bromination amounted to 60% of the theoretical.

Reaction of 1.75 mmole of N-bromosuccinimide residues of PNBS (I) with 0.75 mmole of cumene (II) in 5 ml boiling carbon tetrachloride in the presence of 3.15 mg benzoylperoxide for 1.5 hours resulted in a mixture containing α,β,β' -tribromocumene (III, 48%), β -bromo- α -methylstyrene² (IV, 15%) and α -bromomethylstyrene³ (V, 13%), and unchanged cumene (II, 24%), as shown by analysis of the NMR spectra.⁴ When the molar ratio of I to II was 3.7:1, and the reaction proceeded for 3 hours, the yield of III increased to 85%.

Compound III was isolated from the reaction mixture by thick layer chromatography ($R_f = 0.3$) on Kieselgel GF 254, using petroleum ether as eluent. Anal. Calcd. for $C_9H_9Br_3$: C, 30.25; H, 2.52; Br, 67.23. Found: C, 30.73; H, 2.50; Br, 66.1. Compound III was characterized by its NMR spectrum, which consisted of an AB quartet (4H), δ 4.39, 4.17 ppm ($J = 11$ Hz), and a multiplet, centered at 7.38 ppm (5H) and its mass spectra contained a 3-bromine quartet, M-1 at $m/e = 353$. III was also obtained by bromination of cumene with excess bromine or by addition of bromine to α -bromomethylstyrene (V) in carbon tetrachloride solution.



It is of interest to note that neither α -bromocumene (VI)⁵ nor α,β -di-bromocumene (VII)⁶ were formed upon reacting polymer I with cumene (II) at any of the molar residue ratios of I to II investigated (1:1, 1.2:1, 2.3:1, 3.7:1, respectively). Compounds VI and VII, however, are the only bromination products obtained when cumene is reacted with N-bromosuccinimide (NBS) in boiling carbontetrachloride. For example, when the molar ratio of NBS to cumene was 1:1, the NMR spectrum of the mixture of products indicated the presence of VI (80%), VII (10%) and starting material (10%). Even when the molar ratio of NBS to cumene was increased to 10:1, no α,β,β' -tribromocumene could be detected in the reaction mixture which consisted mainly of VII (95%). A similar behaviour was exhibited by p-cymene and β -bromocumene, which yielded on treatment with PNBS, the corresponding tribromoderivatives. The expected α -bromination products were obtained on treatment with NBS.

The formation of compound III from cumene on treatment with PNBS most likely proceeds by a set of consecutive reactions, the first of which consists of benzylic bromination to yield VI. VI undergoes dehydrobromination to form α -methylstyrene (VIII). The hydrobromic acid formed reacts with the N-Br moiety of the polymer to liberate a bromine molecule, which adds to the double bond of VIII to form VII. Compound VII undergoes further dehydrobromination to form IV and V. Compound III is finally formed by addition of bromine to V. Compound III is stable under the experimental conditions employed and thus accumulates in the reaction mixture.

The dehydrobromination capacity of the maleimide residues of PNBS was checked by refluxing carbon tetrachloride solutions of III, VI and VII in the presence of polymaleimide. When

0.07 ml of a mixture containing III (43%) and VII (50%) was treated with 0.344 g of polymaleimide in 3 ml boiling carbon tetrachloride for 2 hours, analysis of the reaction mixture showed that while the amount of III was essentially unchanged, VII underwent extensive dehydrobromination to yield IV (7% in the reaction mixture) and V (26% in the reaction mixture). No such changes were observed when the same mixture of III and VII was treated with succinimide or kept for 2 hours in boiling carbon tetrachloride. Treatment of 0.1 ml of a mixture containing VI (50%) and VII (26%) with 0.537 gr of polymaleimide in 6 ml of boiling carbon tetrachloride for 2 hours yielded a mixture containing IV (8%), V (15%), VI (6%), VII (3%) and VIII (44%).

α -Methylstyrene (VIII) does not react with PNBS or NBS at the temperature of boiling carbon tetrachloride. At higher temperatures (160-170°C) both PNBS and NBS³ react with VIII to yield V as the major product and IV as the minor product. This leads to the conclusion that if VIII appears as an intermediate in the reaction leading to the formation of III, it adds bromine rather than undergoing allylic bromination. Bromine is thus available only after the dehydrobromination of VI; benzylic bromination is thus a prerequisite step in the formation of III.

Different reaction products were obtained also when ethylbenzene was reacted with PNBS and NBS in boiling carbon tetrachloride and in the presence of free radical initiators. When the molar ratio of NBS residues in I to ethylbenzene was 1.13:1, the NMR spectrum of the mixture of products indicated 40% of α -bromoethylbenzene (compared to 92% using NBS) and 31% of α,β -dibromoethylbenzene (0% with NBS). A molar ratio of PNBS to ethylbenzene of 3.3:1, resulted in 71% of α,β -dibromoethylbenzene. Reactions of NBS with ethylbenzene, in molar ratios of 1:1, 1.5:1 and 2.5:1, respectively did not yield any α,β -dibromoethylbenzene. Cyclohexene, when reacted with PNBS, yielded exclusively 1,2-dibromocyclohexane, while, with NBS, 3-bromocyclohexene was obtained.⁸ Toluene and diphenylmethane, when reacted with PNBS or NBS, yielded benzylbromide and α -bromodiphenylmethane.⁹

It is of interest to note that reaction of NBS in polar medium with the above mentioned benzylic and olefinic compounds, gave similar products to those obtained with PNBS in carbon tetrachloride. Thus, when NBS (3.2 mmole) reacted with cumene (1 mmole) in 3 ml boiling acetonitrile in the presence of 7 mg azobisisobutyronitrile, for 75 min, α,β,β' -tribromocumene (III) was obtained in a yield of 70%. Reaction of NBS with ethylbenzene in acetonitrile yielded α -bromoethylbenzene and also α,β -dibromoethylbenzene. Treatment of VII with NBS in acetonitrile caused dehydrobromination of VII to IV and V.

The unusual reactions of PNBS may be due to its polymeric structure, by which neighbouring groups effect the chemical properties of the active functional groups of the polymer. The N-bromosuccinimide residues on the polymer are located in a polar medium provided by the two succinimide residues adjacent to them. In an alternative copolymer of styrene-maleimide, the N-bromosuccinimide moiety in the polymer will be situated between two styrene residues and should thus not undergo the same polar interactions. Such a copolymer⁹ was prepared and brominated. This brominated copolymer did not yield on reaction with cumene α,β,β' -tribromocumene, nor any α,β -dibromoethylbenzene on reaction with ethylbenzene. The unbrominated copolymer did not dehydrogenate α,β -dibromocumene in boiling carbon tetrachloride.

PNBS can be recovered quantitatively from the reaction mixture, rebrominated and used again either as brominating or oxidating agent.

Acknowledgement. This work was supported by a grant from the Israel National Council for Research and Development.

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