Bromination with *N*, *N*-Dibromobenzenesulfonamide

Suketaka Ito and Toshio Oya

Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Nagano

(Received July 8, 1966)

In connection with the Wohl-Ziegler reaction, there have been already published a large number of reports(1,2) which involve not only the bromination of olefins in the allyl position, but also the side-chain bromination of toluene types, the nuclear bromination of aromatic compounds, the α-bromination of ketones, and other related reactions.

It has been shown that *N*-bromosuccinimide (NBS) is the best brominating agent among the *N*-bromo-imides and -amides of carboxylic acids, and that *N*-bromo-sulfonamides or -imides are unsuitable for this type of reaction(3) because of their property of adding to the double bond rather than introducing a halogen atom in the allyl position of an olefin.(3,4)

However, *N*, *N*-dichloroarenesulfonamides, such as *N*, *N*-dichlorobenzene- or *N*, *N*-dichloro-*p*-toluenesulfonamide, have given fairly good results in the side-chain chlorination of toluene(5); in the nuclear chlorination of acetanilide,(6) phenetole,(7) fluorene(8) and anthracene(9); in the α-chlorination of ethyl acetoacetate,(10) and in the chlorination of cyclohexane,(5) although it produced only a poor result in the allylic chlorination of cyclohexene.(3)

As to *N*, *N*-dibromobenzenesulfonamide, however, there have been few studies of the reactions of this type.

In the present study, with *N*, *N*-dibromobenzenesulfonamide, the bromination of cyclohexene, cyclohexane, cyclohexanone, toluene, diphenylmethane, triphenylmethane, anisole, dimethylaniline and acetanilide were attempted. Carbon tetrachloride was used as the solvent. Since ethers, such as diethyl ether and tetrahydrofuran, react rapidly with *N*, *N*-dibromobenzenesulfonamide to yield certain brominated products, they can not be used for solvents. The resulting benzenesulfonamide in the reaction was readily recoverable as precipitates and could be used again as the starting material of *N*, *N*-dibromobenzenesulfonamide after one or two recrystallizations from ethanol.

N, *N*-Dibromobenzenesulfonamide, as was expected, yielded little of the allyl-brominated product from cyclohexene,(11) but from the other compounds it gave the same products as NBS did, in fairly good yields.

The compounds, the products, the reaction conditions, and the yields are summarized in Table 1. In that table the data on NBS, cited from the literature, are shown in parentheses.

As Table 1 shows, *N*, *N*-dibromobenzenesulfonamide gave as good results as NBS or better in the bromination of cyclohexane, toluene, diphenylmethane, triphenylmethane and anisole. Furthermore, this reagent can be more easily prepared in a high yield and is fairly stable. Therefore, *N*, *N*-dibromobenzenesulfonamide may be a useful brominating agent for the compounds of these types.

Experimental(16)

N, N - Dibromobenzenesulfonamide (DBA-B). This reagent was prepared according to the method described in the literature,(17) mp 114—115°C. It was stored in a desiccator on phosphorus pentoxide in a dark place and used without further purification. The purity of DBA-B was 99.4%, as determined by iodometry according to the method for *N*-bromoacetamide.(18)

---

1) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

2) L. Horner and E. H. Winkelmann, "Newer Methods of Preparative Organic Chemistry," Vol. III, ed. by W. Foerest and translated by H. Birbaum, Academic Press, New York and London (1964), p. 151.

3) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942); *Chem. Abstr.*, **37**, 5032 (1943).

4) Z. Földi, *Chem. Ber.*, **63B**, 2257 (1930); *Chem. Abstr.*, **25**, 687 (1931).

5) T. Takizawa and K. Hoshiai, *Mem. Inst. Sci. Ind. Research, Osaka Univ.*, **7**, 136 (1950).

6) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, **1927**, 986; *Chem. Abstr.*, **21**, 2669 (1927).

7) K. A. Kornev, *Doklady Akad. Nauk S. S. S. R.*, **100**, 1091 (1955); *Chem. Abstr.*, **50**, 2463 (1956).

8) A. E. Kretov and V. V. Litvinov, *Zhur. Obshchei Khim.*, **31**, 1183 (1961); *Chem. Abstr.*, **55**, 23461 (1961).

9) A. E. Kretov and V. V. Litvinov, *ibid.*, **30**, 3028 (1960); *Chem. Abstr.*, **55**, 16501 (1961).

10) A. E. Kretov, *Khim. Nauk*, **1953**, 206; *Chem. Abstr.*, **50**, 16692 (1956).

11) 1, 2-Dibromocyclohexane was obtained in 46% yield.

12) Ng. Ph. Buu-Hoï and P. Demerseman, *J. Org. Chem.*, **18**, 649 (1953).

13) These data were obtained by the authers.

14) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

15) Ng. Ph. Buu-Hoï, *Ann.*, **556**, 1 (1944).

16) The experimental procedures for bromination were represented by two examples.

17) Y. Ueno, *J. Pharm. Soc. Japan*, **72**, 1622 (1952); *Chem. Abstr.*, **47**, 8764 (1953).

18) E. P. Olivets and C. Gerold, "Organic Syntheses," Vol. 31, p. 17 (1951).

TABLE 1. THE BROMINATION WITH *N, N*-DIBROMOBENZENESULFONAMIDE

Compound	Product	Reaction condition*	Yield, %
Cyclohexene	3-Bromocyclohexene	10 min, CCl_4	Trace
		(20 min, CCl_4	87)8)
Cyclohexane	Cyclohexyl bromide	2 hr, Benzoyl peroxide	69.3
		(20 min, Azobisisobutyronitrile	48)12)
Cyclohexanone	2-Bromocyclohexanone	2.5 hr, CCl_4, Benzoyl peroxide	53
		(2 hr, CCl_4, Benzoyl peroxide	58.8)13)
Toluene	Benzyl bromide	10 min, Benzoyl peroxide	80.7
		2 hr, no Catalyst	61.0
		(45 min, CCl_4, Benzoyl peroxide	64)14)
Diphenylmethane	Diphenylmethyl bromide	1 hr, CCl_4 Benzoyl peroxide	73.6
		(1 hr, CCl_4	81)15)
Triphenylmethane	Triphenylmethyl bromide	1 hr, CCl_4, Benzoyl peroxide	82.4
		(5 min, CCl_4	62)15)
Anisole	*p*-Bromoanisole	25 min, CCl_4	89.3
		(16 hr, CCl_4	32)15)
Dimethylaniline	*p*-Bromodimethylaniline	20 min, CCl_4	32
		(1 hr, CCl_4	71)15)
Acetanilide	*p*-Bromoacetanilide	10 min, CCl_4	91
		(1 hr, CCl_4	99)15)

* Reaction time, solvent and catalyst, when it was used, were shown.

The Bromination of Diphenylmethane. A mixture of 15.8 g (0.05 mol) of DBA-B, 16.8 g (0.1 mol) of diphenylmethane, 200 mg of benzoyl peroxide, and 100 m*l* of carbon tetrachloride was refluxed for 1 hr; after the reaction mixture had then been cooled, the separated sulfonamide was removed by filtration. Fractional distillation of the filtrate gave 18.2 g (73.6%) of diphenylmethyl bromide, bp 145—155°C/5 mmHg, which solidified at room temperature. It melted at 40—41°C after recrystallization from *n*-hexane.

The Bromination of Anisole. A mixture of 15.8 g of DBA-B, 10.8 g (0.1 mol) of anisole, and 80 m*l* of carbon tetrachloride was shaken for 10 min and then refluxed for 15 min. Filtration and fractional distillation of the reaction mixture gave 16.7 g (89.3%) of *p*-bromoanisole, bp 108—111°C/24 mmHg; mp 11—12°C, n_D^{21}: 1.5620.