

Short Communication

Pakistan J. Sci. Ind. Res., Vol. 15, Nos. 1-2, February-April 1972

ACTION OF THIONYL BROMIDE ON ORGANIC ACIDS

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(Received September 2, 1971; revised January 13, 1972)

Until recent years, thionyl bromide has been regarded as something of a curiosity and very few references to its use in organic synthesis are to be found in the literature. Although it cannot be used as a general reagent for bromination, owing to its decomposition, it can nevertheless be used with advantage in certain cases, where the use of the classical reagents e.g. hydrogen bromide and phosphorus tribromide, leads to subjection of the material to unduly stringent conditions, which result in unwanted side reactions. Only one instance has been recorded for the use of thionyl bromide for making acid bromides. We decided to investigate the reaction of thionyl bromide with various types of organic acids.

However, thionyl bromide has been used on occasions to replace an alcoholic hydroxyl group by bromine with the formation of an alkyl bromide.^{2,3,4,5}

Saraf⁶ used thionyl bromide to convert phenol into 2,4-dibromophenol (yield 85%) and tropolone into 3,7-dibromotropolone (yield 45%).

Experimental

Pure acids, in quantities of 10-20 g, were treated with two or three times their weight of freshly distilled thionyl bromide. In none of the cases, the reaction was rapid. Usually the mixture had to be warmed from 1 to 3 hr on the water-bath to complete the reaction. The reactions were carried out neat, and in most cases the acid dissolved in the thionyl bromide. In some cases an acid bromide, an expected product, was obtained, in other cases, where the acid was a dibasic one an anhydride was formed (Table 1). These results were in agreement with those of thionyl chloride.⁷ However, in cases of unsaturated dibasic acids, thionyl bromide behaved differently. In our hands, maleic acid, fumaric acid and cinnamic acid, gave, *dl*-dibromosuccinic acid, *meso*-dibromosuccinic acid and 2,3-dibromophenylpropionic acid respectively in almost quantitative yields (Table 2).

The products obtained were purified either by vacuum distillation or by crystallisation.

Succinic anhydride had also been prepared in about 78% yield by the action of thionyl chloride.⁷ In case of thionyl bromide the yield was improved, and the time of the reaction was reduced from 6 hr to 1 hr. The reaction with malonic acid surprisingly gave no identifiable product. Besides the recovered start-

ing material an oil was obtained, which was lachrymatory, and showed the presence of halogen. All attempts to purify the oil were of no use.

On comparing this reaction with thionyl chloride, we found, that our results were unexpected. In case of thionyl chloride, maleic acid gave an anhydride and about fumaric acid there were conflicting reports. Some say that it does not react⁷ where others have reported the isolation of fumaryl dichloride.⁸ Similarly, cinnamic acid has been reported to yield an acid chloride.⁹ Thionyl bromide reacted with these acids over a period of 1-2 hr with the formation of dibromo compounds. The formation of such compounds must be due to the decomposition of thionyl bromide into SO₂, S, and Br₂ and it is this bromine which adds on to the double bond.

The first two acid bromides were purified by distillation and were characterised as anilides. In case of phenylpropionic acid, a reaction took place, but we were unable to isolate any product of the reaction. Phthalic acid, as other dibasic acids, gave an anhydride in high yield (Table 3). It may be mentioned that thionyl chloride behaves in a similar manner with the

TABLE 1. SUBSTITUTED ACETIC ACID.

Acid	Amount (g)	Time (hr)	Product	Yield%
Oxalic	10	6	None	—
Succinic	10	1	Succinic anhydride	85%
Malonic	20	2	Starting material + unidentified oil	

TABLE 2. UNSATURATED ACIDS.

Acid	Time (hr)	Product	Yield%
Maleic	1	<i>dl</i> -dibromosuccinic acid + Maleic anhydride	57% 15%
Fumaric	2	<i>meso</i> -dibromosuccinic acid	85%
Cinnamic	1	2,3-dibromophenylpropionic acid	90%

TABLE 3. SUBSTITUTED BENZOIC ACIDS.

Acid	Time (hr.)	Product	Yield%
<i>p</i> -Toluic	2	<i>p</i> -Toluyyl bromide	45
<i>p</i> -Chlorobenzoic	2	<i>p</i> -Chlorobenzoylbromide	52
Phenylpropionic	3	None	—
Phthalic	1	Phthalic anhydride	90

above-mentioned acids⁷ except in the case of phenylpropionic acid where an acid chloride was obtained. Further work with thionyl bromide is in progress.

Acknowledgement. The authors are grateful to the Drug Research Institute Islamabad, for providing facilities to carry out this work and one of us (Athar Zia) to the Islamabad University for providing the financial assistance.

References

1. A.H. Mayes and Partington, J. Chem. Soc., 2594(1926).
2. A. Mekenzie and T.M.A. Tudhope, J. Biol. Chem., **62**, 551(1924).
3. R. Kühn and T. Wagner-Jauregg, Chem. Ber., **61**, 514 (1928).
4. T. Kenyon, H. Phillips and (Mss) V.P. Pittman, J. Chem. Soc., 1072 (1935).
5. F. Govaert and M. Hansens, Natuurw Tijdscher **21**, 25 (1940).
6. S.D. Saraf, Can. J. Chem., **47**, 2803 (1969).
7. L.M.cMaster and F.F. Ahmann, J. Am. Chem. Soc., **50**, 145 (1928).
8. A.M. Howald and J.L. Jones, Chem. Abstr., **44**, 6198.
9. E.B. Womack and J. Mewhirter, Organic Synthetic Collection, vol. III, 174.