

THE ACTION OF *N*-BROMOSUCCINIMIDE ON ALCOHOLS AND AMINES

BY M. Z. BARAKAT and G. M. MOUSA

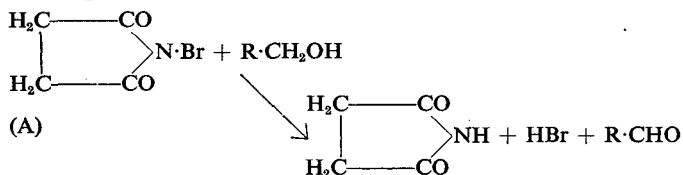
From the Biochemistry Department, Faculty of Medicine, Abbassia, Ibrahim Pasha El-Kebir University, Cairo, Egypt

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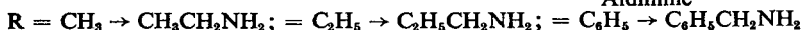
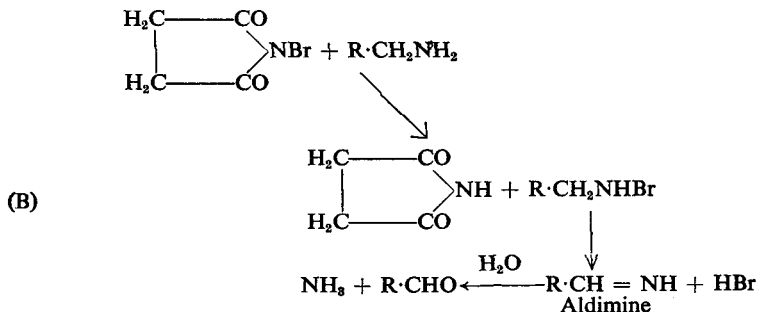
N-CHLOROSUCCINIMIDE has been shown to react vigorously with benzyl alcohol to give benzaldehyde in 74 per cent. yield. Benzhydrol similarly gives the corresponding ketone in 77 per cent. yield.¹

Nothing seems to be known about the reaction mentioned in the title. *N*-Bromosuccinimide reacts readily at room temperature on primary alcohols, e.g., methanol, ethanol and benzyl alcohol, yielding the corresponding aldehydes, formaldehyde, acetaldehyde and benzaldehyde respectively (compare scheme A). In the case of secondary alcohols, e.g., *isopropanol*, the reaction proceeds rapidly at room temperature giving the corresponding ketone, e.g., acetone. The formation of succinimide and hydrobromic acid has been proved in each case.

When *N*-bromophthalimide was allowed to react with benzyl alcohol in aqueous medium, it was found necessary to warm the reaction mixture to effect rapid oxidation.



N-Bromosuccinimide is stable towards water and crystallises from hot water.² This fact eliminates the assumption that hypobromous acid is first formed which subsequently oxidises the alcohol. The aldehydes produced cannot be detected easily by odour, but they are isolated in the form of the 2:4-dinitrophenylhydrazones and identified by the m.pt. and mixed m.pt.



Similarly, it has been found that *N*-bromosuccinimide reacts readily with primary amines (e.g., ethylamine, *n*-propylamine and benzylamine) at room temperature in an aqueous medium giving the corresponding aldehydes, acetaldehyde, propionaldehyde and benzaldehyde respectively (compare scheme B). The ammonia liberated in the reaction is present as ammonium bromide.

In the case of amines, the aldehydes have also been isolated as the 2:4-dinitrophenylhydrazones and identified by the m.pt. and mixed m.pt. The formation of succinimide and ammonia has been proved.

The fact that *N*-bromosuccinimide reacts readily on alcohols and primary amines at room temperature provides a new reagent for the detection of these compounds.

EXPERIMENTAL

Action of N-Bromosuccinimide on Alcohols. *N*-Bromosuccinimide (2 g.) and methanol (5 ml.), or ethanol (6 ml.) or *isopropanol* (7 ml.), or benzyl alcohol (4 ml.) were mixed together at room temperature for 10 minutes with occasional shaking; a vigorous reaction took place with the formation of an orange red colour. The mixture must be cooled as the reaction is exothermic, especially in the case of *isopropanol* and benzyl alcohol. After cooling, the reaction mixture was filtered from any unchanged *N*-bromosuccinimide. To the clear filtrate excess of 2:4-dinitrophenylhydrazine hydrochloride in aqueous ethanol was added, giving respectively formaldehyde 2:4-dinitrophenylhydrazone 1.1 g.), acetaldehyde 2:4-dinitrophenylhydrazone (1.3 g.), acetone 2:4-nitrophenylhydrazone (1.2 g.) and benzaldehyde 2:4-dinitrophenylhydrazone (2.2 g.).

Similar experiments were carried out using the similar quantities of *N*-bromosuccinimide and each alcohol and, after the reaction was complete, the filtrate was concentrated to a small bulk (about 2 ml.). After cooling, a white crystalline precipitate was formed, which was filtered and proved to be succinimide (0.8 g.). The presence of hydrobromic acid in the filtrate of the reaction mixture was proved by the silver nitrate test.

Action of N-Bromophthalimide on Benzyl alcohol. *N*-Bromophthalimide (0.50 g.), benzyl alcohol (0.50 g.) and water (10 ml.) were heated gently under a reflux condenser at about 90° C. for 3 minutes, whereupon a vigorous reaction took place. The mixture was then allowed to cool with continuous shaking and was filtered, yielding a filtrate (A) and a solid (B). (B) was crystallised from ethanol and proved to be phthalimide. (A) was treated with excess of 2:4-dinitrophenylhydrazine hydrochloride in aqueous ethanol, whereupon orange crystals were formed. The mixture was allowed to stand in ice for 1 hour, and the deposit was crystallised from ethanol and proved to be benzaldehyde 2:4-dinitrophenylhydrazone; yield about 30 per cent.

Action of N-Bromosuccinimide on Primary Amines. *N*-Bromosuccinimide (2 g.) and ethylamine 33 per cent. aqueous solution (3 g.), or *n*-propylamine (1.2 g.), or benzylamine (0.5 g.) in 6 ml. of water were

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mixed together at room temperature (18° C.) for 10 minutes with frequent shaking. A vigorous reaction took place with the formation of a red colour. The mixture was cooled in ice during the gradual addition of *N*-bromosuccinimide because the reaction was exothermic. After cooling, the mixture was filtered from any unchanged *N*-bromosuccinimide and to the clear filtrate, excess of 2:4-dinitrophenylhydrazine hydrochloride in aqueous ethanol was added, whereupon an orange precipitate was formed, allowed to stand in ice for $\frac{1}{4}$ hour, filtered off and crystallised from ethanol giving acetaldehyde 2:4-dinitrophenylhydrazone, propionaldehyde 2:4-dinitrophenylhydrazone and benzaldehyde 2:4-dinitrophenylhydrazone respectively. Yield about 40 per cent.

Similar experiments using similar quantities of *N*-bromosuccinimide and each amine were carried out and the clear filtrate concentrated to a small bulk (2 ml.) and allowed to cool. On standing, colourless crystals separated which proved to be succinimide (1 g.). The formation of ammonia during the reaction was also proved, after rendering the filtrate alkaline with sodium hydroxide (20 per cent.), by the dense white fumes obtained when a glass rod moistened with a drop of concentrated hydrochloric acid was held at the mouth of the test-tube containing the reaction mixture.

SUMMARY

(1) *N*-Bromosuccinimide converts primary alcohols at room temperature into the corresponding aldehydes, e.g., ethanol into acetaldehyde. Secondary alcohols are similarly oxidised to the corresponding ketones, e.g., isopropanol gives acetone.

(2) *N*-Bromosuccinimide reacts vigorously with primary amines in an aqueous medium at room temperature to give the corresponding aldehydes, e.g., benzylamine yields benzaldehyde.

(3) *N*-Bromosuccinimide is a new reagent for the detection of primary alcohols, secondary alcohols and primary amines. *N*-Bromophthalimide behaves similarly with primary alcohols, e.g., benzyl alcohol, but requires warming to effect oxidation.

REFERENCES

1. Hebbelynck and R. H. Martin, *Experientia*, 1949, 5, 69.
2. Lamchen, *J. chem. Soc.*, 1950, 747.