trum between 220 and 600 mμ was read in a DU Beckman spectrophotometer.

DEPARTMENT OF RADIATION BIOLOGY AND
DEPARTMENT OF BIOCHEMISTRY
SCHOOL OF MEDICINE AND DENTISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

---

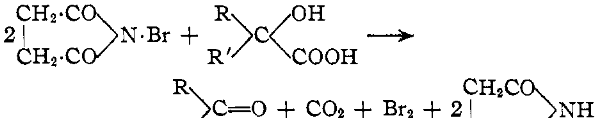
## Action of N-Bromosuccinimide on Aliphatic α-Hydroxy Acids

BY MOHAMED ZAKI BARAKAT AND MOHAMED FATHY ABD EL-WAHAB

RECEIVED MAY 4, 1953

It has already been shown that N-bromosuccinimide functions as an oxidizing agent, *e.g.*, it converts primary and secondary alcohols into the corresponding aldehydes and ketones, respectively,[1,2] and in many cases the action is highly selective. Fieser and Rajagopalan have reported high selectivity in the oxidation of the 7α-hydroxyl group of cholic acid and the 6β-hydroxyl group of cholestane-3β,5α,6β-triol by use of N-bromosuccinimide. Whereas 3-hydroxyl groups usually resist attack by N-bromosuccinimide in aqueous acetone, methyl 3α-hydroxy-9α,11α-oxidocholanate[3] is oxidized to the 3-ketone. Selective oxidation of a 3-acyl derivative of methyl cholate[4] to the 7-ketone can be accomplished in high yield with N-bromosuccinimide.

There appears to have been no report on the action of this reagent with α-hydroxy acids. We have shown that N-bromosuccinimide reacts readily on heating in an aqueous solution with aliphatic α-hydroxy acids, *e.g.*, glycolic, lactic, mandelic and benzilic acids, yielding aldehydes or ketones containing one carbon atom less, *e.g.*, formaldehyde, acetaldehyde, benzaldehyde and benzophenone, respectively. Evolution of carbon dioxide and bromine was demonstrated in all cases. Succinimide has been isolated in the reaction with lactic and benzilic acids.



$$2\,(CH_2\cdot CO)_2N\cdot Br + RR'C(OH)COOH \longrightarrow RR'C{=}O + CO_2 + Br_2 + 2\,(CH_2CO)_2NH$$

R = R′ = H : glycolic acid ⟶ formaldehyde
R = $CH_3$, R′ = H : lactic acid ⟶ acetaldehyde
R = $C_6H_5$. R′ = H : mandelic acid ⟶ benzaldehyde
R = R′ = $C_6H_5$: benzilic acid ⟶ benzophenone

Compared with the fatty acids the corresponding α-hydroxy acids possess higher dissociation constants, and this may explain why such a reaction takes place; an analogous case may be the degradation of aliphatic dicarboxylic acids, *e.g.*, oxalic acid,[5] by N-bromosuccinimide in aqueous medium at room temperature.

The conversion of benzilic acid to benzophenone when treated with N-bromosuccinimide provides a new route to pass from α-diketones, *e.g.*, benzil, to aromatic ketones, *e.g.*, benzophenone.

### Experimental

**Action of N-Bromosuccinimide on Aliphatic α-Hydroxy Acids.** (1) **Isolation of Aldehydes.** (a).—N-Bromosuccinimide (1.78 g., 2 moles) and glycollic acid (0.38 g., 1 mole) or lactic acid (0.43 cc., 1 mole) or mandelic acid (0.76 g., 1 mole) in distilled water (20 cc.) were refluxed in the apparatus previously described (Schonberg, Moubasher and Mostafa[6]) in a stream of carbon dioxide for 20 minutes. The receiver contained an ice-cold solution of 2,4-dinitrophenylhydrazine sulfate (0.6 g.) in alcohol (20 cc.). Yellow or orange crystals deposited and were recrystallized from the proper solvent (ligroin, alcohol and ethyl acetate) to give the 2,4-dinitrophenylhydrazone of formaldehyde, acetaldehyde and benzaldehyde, respectively, in 50% yields, identified by their m.p. and mixed m.p. with authentic samples.

(b) **Formation of Bromine, Carbon Dioxide and Succinimide in the Degradation.**—N-Bromosuccinimide (1.78 g.) and lactic acid (0.43 cc.) in distilled water (20 cc.) were heated for 20 minutes; the mixture was then concentrated by heat to a small volume (about 2 cc.) and allowed to cool; the colorless crystals which deposited were pressed on a porous plate and recrystallized from benzene. They were proved to be succinimide by m.p. and mixed m.p. (yield 0.5 g.).

The evolution of bromine and carbon dioxide during the degradation was demonstrated by passing the gases evolved during the reaction, first into 10% silver nitrate solution acidified with nitric acid and then into baryta water. A yellowish-white precipitate of silver bromide deposited, while the baryta water became turbid.

(2) **Isolation of Ketones.**—It is sufficient to describe one example in detail to illustrate the procedure.

N-Bromosuccinimide (1.78 g., 2 moles) and benzilic acid (1.14 g., 1 mole) in distilled water (100 cc.) were refluxed for 30 minutes. The reaction started after heating for 2 minutes with evolution of bromine vapor. The N-bromosuccinimide and benzilic acid gradually dissolved and an oil began to separate. At the end of the reaction, the mixture was allowed to cool and extracted with ether. The aqueous layer was concentrated to a small volume (about 5 cc.) and on standing deposited colorless crystals of succinimide, which after recrystallization from benzene were identified by m.p. and mixed m.p. (yield 0.6 g.).

The ethereal layer was dried over anhydrous sodium sulfate for 12 hours, filtered and concentrated to yield an oil which soon crystallized. The solid was recrystallized from aqueous alcohol to give benzophenone (m.p. and mixed m.p.) in 85–90% yield. The evolution of carbon dioxide during the reaction was demonstrated as above.

**Acknowledgment.**—The authors thank Dr. M. M. El-Sadr for his interest in this work and acknowledge their gratitude to the National Aniline Division, New York 6, New York, for supplying N-bromosuccinimide.

---

[1] L. F. Fieser and S. Rajagopalan. THIS JOURNAL. **71**. 3935 (1949): *ibid.*. **71**, 3938 (1949).

[2] M. Z. Barakat and G. M. Mousa. *J. Pharm. and Pharmacol.*. **4**, 115 (1952).

[3] L. F. Fieser, H. Heymann and S. Rajagopalan, THIS JOURNAL, **72**. 2306 (1950).

[4] L. F. Fieser and S. Rajagopalan. *ibid.*, **72**, 5530 (1950).

[5] M. Z. Barakat, *J. Pharm. and Pharmacol.*, **4**, 582 (1952).

[6] Schönberg. Moubasher and Mostafa. *J. Chem. Soc.*. 176 (1948).

BIOCHEMISTRY DEPARTMENT
IBRAHIM PASHA EL-KEBIR UNIVERSITY
FACULTY OF MEDICINE
ABBASSIA, CAIRO, EGYPT

---

## The High Field Conductance of Aqueous Solutions of Ammonia at 25°[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

RECEIVED JULY 6. 1953

The high field conductance of aqueous solutions of ammonia, between 1.3 and 1.5 × $10^{-3}$ *M*, has been measured at 25.00° relative to potassium chloride. The high field conductance data are

---

[1] Contribution No. 1166 from the Department of Chemistry, Yale University.