

## Complex Metal Hydride Reactions. II.<sup>1</sup> Reduction of 1-Hydroxymethyl- and 1-Benzoyloxy-methyl-1*H*-benzotriazole<sup>2</sup>

NORMAN G. GAYLORD AND DANIEL J. KAY

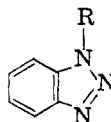
Received April 16, 1958

The reduction of compounds containing the  $\begin{array}{c} | \\ | \\ \text{---NCO---} \\ | \end{array}$  grouping, with lithium aluminum hydride, generally results in cleavage of the carbon-oxygen bond.<sup>3</sup> This cleavage has been observed whether the grouping was present in the original compound, as in oxazolidines, or resulted from the initial reduction of a carbon-nitrogen double bond in the  $\begin{array}{c} | \\ \text{---N=C---O---} \\ | \end{array}$  grouping, as in various heterocyclic compounds.<sup>1</sup> The cleavage of the  $\begin{array}{c} | \\ | \\ \text{---NCO---} \\ | \end{array}$  grouping in various heterocyclic carbinolamines with sodium borohydride also occurs at the carbon-oxygen bond.<sup>4</sup>

An attempt to carry out the reduction of 1-hydroxymethyl-1*H*-benzotriazole (I) with lithium aluminum hydride in a dioxane-ether-benzene mixture resulted in the immediate precipitation of the complex resulting from the reaction of the complex metal hydride and the active hydrogen, and I was recovered from the reaction mixture.<sup>5</sup> The reduction of 1-benzoyloxymethyl-1*H*-benzotriazole (II) with lithium aluminum hydride in an ether-tetrahydrofuran mixture gave 93% of benzyl alcohol, 17% of I and 47% of 1*H*-benzotriazole (III). None of the expected 1-methyl-1*H*-benzotriazole was isolated. Reduction of the ester group in II would be expected to yield benzyl alcohol and I. The insoluble intermediate complex from I resists further reaction.

The isolation of III indicates that cleavage of the  $\begin{array}{c} | \\ | \\ \text{---NCO---} \\ | \end{array}$  grouping occurred at the nitrogen-carbon linkage rather than the expected carbon-oxygen linkage. This is the first reported case of a cleavage in this direction and is analogous to the reductive cleavage of *N*-acylated heterocyclic compounds with aromatic character to yield the heterocyclic amine and alcohols or aldehydes.<sup>6</sup> The methyl ben-

zoate which should accompany III as a result of the scission is apparently further reduced to benzyl alcohol.

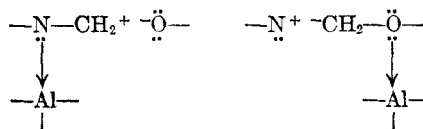


- I, R = CH<sub>2</sub>OH  
 II, R = CH<sub>2</sub>OCOC<sub>6</sub>H<sub>5</sub>  
 III, R = H

The reduction of I with sodium borohydride in ethanol solution gave 61% of III. Reduction of II gave 78% of III and 55% of methyl benzoate. The latter is isolated as a result of the non-reduction of esters by sodium borohydride.

In the reduction of 1-benzoylbenzotriazole, as well as other *N*-acyl heterocyclics, to the amine and the aldehyde or alcohol, it has been proposed that the decreased electron-donating tendency of the nitrogen atom coupled with the polarization of the carbonyl group, results in the carbon atom assuming a more positive character. The nucleophilic attack by the negative hydride or aluminohydride ion on the carbon atom results in a displacement of the nitrogen.<sup>7</sup> In the reduction of the *N*-methylol and *N*-benzoyloxymethyl derivatives, the decreased electron-donating tendency of the nitrogen atom resulting from stabilization as a result of the aromatic character of the benzotriazole nucleus, and the absence of polarization of a carbonyl group, makes the nitrogen atom the more positive center. Nucleophilic attack by the hydride, aluminohydride or borohydride anion on the nitrogen atom results in a displacement of the carbon atom.

An alternative explanation, distinguishing between the carbon-oxygen bond cleavage, which occurs in all examples reported to date, and the nitrogen-carbon bond cleavage, reported herein, involves the tendency of the nitrogen and oxygen atoms to coordinate with the aluminum or boron of the complex hydride anion. The coordination of the nitrogen with the metal atom would result in a weakening of the carbon-oxygen bond, possibly to the extent of ionization. The coordination of the oxygen with the metal atom would result in a weakening of the nitrogen-carbon bond.



The attack of the hydride or complex hydride anion on the positive center would result in the indicated displacement. Normally, coordination with the nitrogen would be the most likely process. However, where such coordination is sterically hindered or decreased by resonance stabilization of

(1) Part I, *J. Am. Chem. Soc.*, **78**, 2167 (1956).

(2) Reactions of Carbinolamines. III. Part II, *J. Org. Chem.*, **22**, 1022 (1957).

(3) (a) N. G. Gaylord, *Experientia*, **10**, 351 (1954); (b) *Reduction with Complex Metal Hydrides*, Interscience Publishers, New York, 1956, p. 807.

(4) S. Bose, *J. Indian Chem. Soc.*, **32**, 450 (1955).

(5) N. G. Gaylord, *J. Am. Chem. Soc.*, **76**, 285 (1954).

(6) Ref. 3b, p. 586.

(7) N. G. Gaylord, *Experientia*, **10**, 423 (1954).

the electron pair of the nitrogen atom, coordination with the oxygen atom occurs preferentially.

Further work on the reduction of the *N*-substituted heterocyclics with aromatic character is in progress.

#### EXPERIMENTAL

**Reduction of II with lithium aluminum hydride.** A suspension of 10 g. (0.04 mole) of II<sup>2</sup> in 330 ml. of ether was added over 50 min. to a solution of 4 g. of lithium aluminum hydride in 250 ml. of ether. The milky white suspension was refluxed for 1 hr. before standing overnight. A grayish deposit covered with a fine white solid separated during the standing period. A total of 100 ml. of tetrahydrofuran was added and the mixture was refluxed for an additional 2 hr. Decomposition was carried out with 4 ml. of water, 4 ml. of 15% sodium hydroxide, and 12 ml. of water, in that order. The mixture was filtered and the filter cake washed with ether. The combined solvent extracts were washed with a saturated solution of sodium carbonate and the solvent phase dried over magnesium sulfate. Acidification and concentration of the sodium carbonate wash solution failed to yield any organic product. Concentration of the dried solvent phase produced 4 g. (93% yield) of benzyl alcohol, identified by its physical constants and the identity of its phenylurethan with an authentic specimen.

The filter cake was extracted in a Soxhlet extractor with benzene. Concentration of the benzene extract failed to yield any product. Extraction of the filter cake with dioxane gave 1 g. of solid having a m.p. above 210°. Flame ignition of a sample indicated a non-organic content. Extraction of the filter cake with ethyl acetate yielded 0.4 g. of a similar solid. The solid was dissolved in water and acidified to yield 1 g. (17% yield) of I, m.p. 149°. I gave the picrate of 1*H*-benzotriazole, m.p. 171–172° (reported<sup>6</sup> m.p. 173–174°).

The filter cake was suspended in water and acidified until a clear solution was obtained. The aqueous solution was extracted with 3 × 100 ml. portions of ethyl acetate, followed by concentration of the organic extracts to dryness. A total of 22 g. (46.8%) of 1*H*-benzotriazole, m.p. and mixed m.p. 95–97° (reported<sup>6</sup> m.p. 97–99°), was isolated.

**Reduction of I with sodium borohydride.** A solution of 10 g. (0.067 mole) of I in 200 g. of ethanol was added over 15 min. to a solution of 4.4 g. (0.116 mole) of sodium borohydride in 125 g. of ethanol. The clear reaction mixture was maintained at 35–40° during the addition and for an additional 1.5 hr. Decomposition was carried out with 25 ml. of water and the pH was adjusted to 7 with dilute hydrochloric acid. The mixture was filtered and the filtrate was concentrated to yield a white solid which was recrystallized from water. A total of 4.9 g. (61.5%) of benzotriazole was obtained.

**Reduction of II with sodium borohydride.** A solution of 10 g. (0.039 mole) of II in 175 g. of ethanol was added over a period of 10 min. to a solution of 2 g. of sodium borohydride in 75 g. of ethanol. The clear reaction mixture was maintained at 35–40° during the addition and for an additional 2 hr. Decomposition was carried out with 20 ml. of water and the pH was adjusted to 5 with dilute hydrochloric acid. After filtration the filter cake was washed with 25 ml. ethanol and the wash liquors were combined with the filtrate. The filtrate was concentrated and the residual oil and solid were taken up in ether and extracted with dilute hydrochloric acid. The dried ether layer was distilled to yield 2.9 g. (54.7%) of methyl benzoate, identified by physical constants and infrared spectrum. The aqueous acid extract was neutralized and on cooling gave 3.6 g. (78%) of benzotriazole.

CENTRAL RESEARCH LABORATORIES  
INTERCHEMICAL CORP.  
432 W. 45th Street  
NEW YORK 36, N. Y.

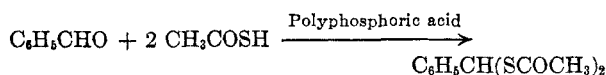
## Phenylmethanedithiol Diacetate<sup>1</sup>

LAMAR FIELD AND CHARLES B. HOELZEL

Received April 17, 1958

Behringer and Grunwald recently described a series of diesters of *gem*-dithiols which had the general structure RCH(SCOR')<sub>2</sub>.<sup>2</sup> Their study of preparations and properties was confined to symmetrical esters in which R and R' were identical, presumably because they were interested chiefly in the catalyzed conversion of thio acids, alone, to such esters.

Prior to their report, we had prepared phenylmethanedithiol diacetate in yields of about 60% by reaction of thioacetic acid, benzaldehyde, and polyphosphoric acid.



Although Behringer and Grunwald mentioned a synthesis of 1,1-propanedithiol dipropionate from thiopropionic acid, propionaldehyde, and phosphorus pentoxide, description also seemed desirable of our work, since it illustrates the use of polyphosphoric acid, probably a milder condensing agent, and extends the method to the preparation of an unsymmetrical ester.

Phenylmethanedithiol diacetate melts at about 37–38°<sup>3</sup> rather than at 147–148°.<sup>4</sup> It has an infrared spectrum resembling those of alkyl thioacetates,<sup>5</sup> and it acylates aniline under mild conditions<sup>6</sup> but not *p*-nitroaniline which (like 2,4-dinitrophenylhydrazine)<sup>2</sup> evidently is too weakly basic.

Application of the method to cyclohexanone gave unpromising results; the distilled product had a wide range of boiling point and refractive index and differed in analysis by several per cent from the values calculated for 1,1-cyclohexanedithiol diacetate.

#### EXPERIMENTAL<sup>7</sup>

Thioacetic acid (6.32 g.) was added in one portion with stirring to 8.0 g. of benzaldehyde cooled in an ice bath. After 2 hr. of stirring, the mixture began to solidify and was allowed to warm to a mushy consistency, after which stirring was continued for 2 hr. The mixture was then completely immersed again in the ice bath and polyphosphoric

(1) Research supported by the Office of Ordnance Research, U. S. Army.

(2) H. Behringer and G. F. Grunwald, *Ann.*, **600**, 23 (1956).

(3) T. L. Cairns, G. L. Evans, A. W. Larchar, and B. C. McKusick, *J. Am. Chem. Soc.*, **74**, 3982 (1952).

(4) J. Bongartz, *Ber.*, **19**, 1934 (1886).

(5) L. H. Noda, S. A. Kuby, and H. A. Lardy, *J. Am. Chem. Soc.*, **75**, 913 (1953).

(6) Cf. R. Schwyzer, *Helv. Chim. Acta*, **36**, 414 (1953).

(7) Melting points are corrected and boiling points uncorrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.