

sis products which were found in the expected positions of glyceric acid and glycolic acid.<sup>5</sup>

The radioactive sugar was epimerized in pyridine.<sup>6</sup> Co-chromatography of the resultant mixture<sup>7</sup> with ribose and arabinose showed identity of the two major radioactive products with the added sugars. The radioactive 2,4-dinitrophenylsazone<sup>8</sup> of D-arabinose was prepared with a tracer quantity of the labeled ribulose. It was found to have the calculated specific activity and this was undiminished by repeated recrystallizations from methyl cellosolve.

The radioactive sugar was catalytically hydrogenated with Adams catalyst and the product was found to co-chromatograph with added ribitol but not with arabitol.

The foregoing observations lead to the conclusion that the radioactive compounds isolated from plants are ribulose 1,5-diphosphate and monophosphate. An examination of the kinetics of formation of this compound from C<sup>14</sup>O<sub>2</sub> during steady state photosynthesis and a discussion of its importance as a C<sub>2</sub> donor in the cycle for regeneration of the CO<sub>2</sub>-acceptors will be published.

(5) Phosphoglycolic acid observed as a minor radioactive product of C<sup>14</sup>O<sub>2</sub> photosynthesis has been separated and identified. Oxidation during chromatography may provide one source of this phosphoglycolic acid.

(6) O. T. Schmidt and R. Treiber, *Ber.*, **66B**, 1765 (1933).

(7) The equilibrium mixture of epimers is known to be largely ribose and arabinose (P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **102**, 563 (1933)). Small amounts of radioactive ribose observed in isolations of ribulose may indicate that it is also present in the original phosphate esters.

(8) C. Nenberg and E. Strauss, *Arch. Biochem.*, **11**, 457 (1946).

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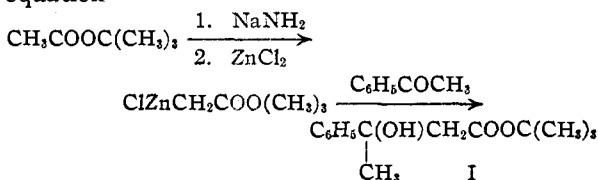
A. A. BENSON

RECEIVED MAY 9, 1951

### β-HYDROXY ESTERS FROM KETONES AND ESTERS

Sir:

We have simulated the Reformatsky type of reaction employing *t*-butyl acetate instead of an α-halo ester in accordance with the following equation



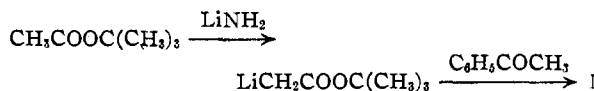
*t*-Butyl acetate was converted to its sodio derivative by means of sodium amide in liquid ammonia, the liquid ammonia replaced by ether, and an ether solution of anhydrous zinc chloride added at -70°. After stirring forty minutes at this temperature, acetophenone was added and the mixture refluxed two hours. There was obtained a 31% yield of *t*-butyl β-hydroxy-β-phenylbutyrate (I), b.p. 124-127° at 4.5 mm. *Anal.*<sup>1</sup> Calcd. for C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>: C, 71.16; H, 8.53. Found: C, 70.77; H, 8.22. Acid hydrolysis and dehydration yielded β-methylcinnamic acid, m.p. and mixed m.p. with an authentic sample, 97-98°.<sup>2</sup>

(1) Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

(2) Rupe and Busolt, *Ber.*, **40**, 4538 (1907).

In a similar manner, *t*-butyl acetate condensed with cyclohexanone and benzaldehyde to form *t*-butyl 1-hydroxycyclohexylacetate (34% yield, b.p. 132-136° at 18 mm. *Anal.*<sup>1</sup> Calcd. for C<sub>12</sub>H<sub>22</sub>O<sub>3</sub>: C, 67.35; H, 10.36. Found: C, 67.24; H, 10.02), and *t*-butyl β-hydroxy-β-phenylpropionate (58% yield, b.p. 154-158° at 10 mm. *Anal.*<sup>1</sup> Calcd. for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>: C, 70.33; H, 8.17. Found: C, 69.98; H, 7.83), respectively.

We have further found that this type of aldol condensation may be effected more conveniently and in higher yield by means of lithium amide (without the use of zinc chloride).



The lithium derivative of *t*-butyl acetate was prepared with lithium amide in liquid ammonia, the ammonia replaced by ether, and the acetophenone added immediately. After refluxing two hours, the hydroxy ester (I), b.p. 111-112.5° at 2 mm. was isolated in 76% yield.

This aldol condensation using lithium amide is particularly striking since use of sodium amide under similar conditions failed to give hydroxy ester.

These important types of aldol condensations are being investigated more thoroughly, employing various lithium and other metallic reagents. The results promise to be of both theoretical interest and of practical value.

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RECEIVED APRIL 24, 1951

(3) Carbide and Carbon Chemicals Fellow.

### THE HEAT OF DISSOCIATION OF NITROGEN\*

Sir:

In recent publications<sup>1,2,3,4</sup> each of the four spectroscopically acceptable nitrogen dissociation energies, 7.383, 8.573, 9.764 and 11.8 e.v. has been again recommended as the correct one. The study of stationary detonation waves provides information on equilibria at high temperatures because Zeldovitch<sup>5</sup> and v. Neumann<sup>6</sup> conclusively show on solid hydro-thermodynamic basis that the properties of an infinite plane wave without rarefaction are determined by the state of complete thermodynamic equilibrium of explosion products. The experimental problem consists largely in adducing the proof that a finite wave has the same velocity as the ideal one. We had been thus engaged to redetermine the heats of sublimation of carbon and of the dissociation of nitrogen when a paper by Döring and Schön appeared.<sup>7</sup> They compare the calculated

\* This research was made possible by funds extended Harvard University under ONR Contracts M50ri-76 to XIX NR-053-094.

(1) L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 359 (1949).

(2) L. Brewer, L. K. Templeton and F. A. Jenkins, *THIS JOURNAL*, **73**, 1462 (1951).

(3) A. G. Gaydon, "Dissociation Energies," Chapman and Hall, London, 1947.

(4) G. Glockler, *J. Chem. Phys.*, **19**, 124 (1951).

(5) Ya. B. Zeldovich, *J. Exp. Theor. Phys. (USSR)*, **10**, 542 (1950).

(6) J. v. Neumann, OSRD Report No. 649, May, 1942.

(7) W. Döring and G. Schön, *Z. Elektrochem.*, **54**, 281 (1950).