diaminoperfluoroalkyl-*s*-triazines listed in Table I, unless otherwise noted. A mixture of 3.86 g. (0.02 mole) of *n*-butylbiguanide hydrochloride, 1.18 g. (0.02 mole) of sodium methoxide, 2.76 g. (0.022 mole) of methyl trifluoroacetate, and 75 ml. of methanol was stirred at room temperature for 4 days, and then drowned in an excess of water. The white crystalline solid which formed from the initial oil weighed 2.75 g. (58.5%) and melted 98–100 .

Anal. Calcd. for $C_8H_{12}F_3N_5$: C, 40.9; H, 5.14; N, 29.8. Found: C, 41.1; H, 5.19; N, 29.6.

Acknowledgment. The authors wish to thank R. K. Madison for his helpful assistance, J. L. Gove for the infrared absorption data and O. E. Sundberg and his associates for the microanalyses.

RESEARCH DEPARTMENT
ORGANIC CHEMICALS DIVISION
AMERICAN CYANAMID COMPANY
BOUND BROOK, N. J.

Reduction of Allylic Halides by Lithium Aluminum Hydride[1]

LEWIS F. HATCH AND RONALD E. GILBERT[2]

Received June 11, 1959

The lithium aluminum hydride reduction of an allylic halide to the corresponding hydrocarbon has been used as a means of identification and characterization of allylic halides, especially geometrical isomers.[3] There is retention of configuration and no allylic rearrangement with this reaction when the allylic halogen atom is terminal. It has been noted, however, that 2,3,3-trichloro-1-butene gives *trans*-2,3-dichloro-2-butene[4] and 3,4-dibromo-1-butene gives *trans*-2-butene.[5] DeWolf and Young have suggested that this reaction goes by an S_N2' mechanism[6] and the conformational implications of this mechanism have been discussed by Hatch, Gardner and Gilbert.[5] This reaction has now been extended to include 3,4-dichloro-1-butene and two secondary-mono-allylic halides (3-chloro-1-butene and 3-bromo-1-butene).

The reduction of 3,4-dichloro-1-butene by lithium aluminum hydride in tetrahydrofuran gave the expected *trans*-2-butene as indicated by gas-liquid partition chromatography. 3-Chloro-1-butene was prepared along with its allylic isomer, *trans*-1-chloro-2-butene, by the addition of hydrogen chloride to butadiene using concentrated hydrochloric acid.[7] Lithium aluminum hydride reduction of this chloride produced a mixture of hydrocarbons containing *cis*-2-butene (5%), butadiene (8%), *trans*-2-butene (18%) and 1-butene (69%). A similar mixture was obtained from 3-bromo-1-butene. The 3-bromo-1-butene was prepared by allylic rearrangement of *trans*-1-bromo-2-butene.

From these data it would appear that the prediction that secondary allylic halides react by an S_N2' mechanism[5] must be modified. The present indications are that at least one other halogen atom is required to be in the vicinity of the secondary allylic halogen to cause the reaction to go exclusively by this mechanism. The other halogen atom or atoms are also required for the reaction to be stereospecific.[5] The butadiene was formed by dehydrohalogenation caused by the lithium aluminum hydride.

Both *trans*-1-chloro-2-butene (crotyl chloride) and *trans*-1-bromo-2-butene (crotyl bromide) give *trans*-2-butene on reduction with lithium aluminum hydride. 1,4-Dichloro-2-butene prepared by the addition of chlorine to butadiene also gave the expected *trans*-2-butene[8] but a purchased sample of 1,4-dichloro-2-butene formed a mixture of products containing 71% *cis*-2-butene and 29% *trans*-2-butene. This dichloride apparently was produced from 1,4-butyndiol by catalytic hydrogenation followed by conversion of the diol to the corresponding dichloride.

EXPERIMENTAL

3,4-Dichloro-1-butene. This dichloride was purchased from Columbia Organic Chemicals, Inc., Columbia, S.C., and purified by distillation: b.p. 42° (40 mm.); n_D^{25} 1.4615. Lit.[9] b.p. 123° (766 mm.); n_D^{20} 1.4630.

1,4-Dichloro-2-butene. A sample of 1,4-dichloro-2-butene was purchased from Columbia Organic Chemicals, Inc., and distilled: b.p. 72.5° (39 mm.); n_D^{25} 1.4872.[8] *cis* isomer b.p. 152.5° (758 mm.), n_D^{25} 1.4887; *trans* isomer b.p. 155.5° (758 mm.), n_D^{25} 1.4871. *trans*-1,4-dichloro-2-butene was synthesized along with 3,4-dichloro-1-butene by the addition of chlorine (45 g., 0.64 mole) to butadiene (31 g., 0.58 mole) in 200 ml. of chloroform at ice bath temperature. The 1,4-dichloro-2-butene was separated from its isomer by distillation: b.p. 74° (40 mm.); n_D^{25} 1.4863.

3-Chloro-1-butene and 1-chloro-2-butene. A mixture of 3-chloro-1-butene and *trans*-1-chloro-2-butene (crotyl chloride) was obtained by the treatment of butadiene (54 g., 1.00 mole) with an excess of 37% hydrochloric acid saturated with hydrogen chloride.[7] The reaction was carried out in a sealed tube at 25° for 36 hr. The organic layer was washed with a dilute sodium bicarbonate solution, dried and distilled. 3-Chloro-1-butene: b.p. 64° (760 mm.); n_D^{27} 1.4111. Lit.[7] b.p. 63.7° (748 mm.); n_D^{20} 1.4151.

trans-1-Chloro-2-butene: b.p. 84° (760 mm.); n_D^{27} 1.4292. Lit.[7] b.p. 84.8° (752 mm.); n_D^{25} 1.4327.

3-Bromo-1-butene. 3-Bromo-1-butene was obtained as a mixture with *trans*-1-bromo-2-butene by permitting the

---

(1) Presented in part at the 136th meeting of the American Chemical Society, Atlantic City, September 13–18, 1959.

(2) Present address: The Dow Chemical Company, Freeport, Texas.

(3) L. F. Hatch and R. H. Perry, *J. Am. Chem. Soc.*, **71**, 3262 (1949).

(4) L. F. Hatch and J. J. D'Amico, *J. Am. Chem. Soc.*, **73**, 4393 (1951).

(5) L. F. Hatch, P. D. Gardner and R. E. Gilbert, *J. Am. Chem. Soc.*, **81**, 5943 (1959).

(6) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

(7) L. F. Hatch and S. S. Nesbit, *J. Am. Chem. Soc.*, **72**, 727 (1950).

(8) K. Mislow and H. M. Hellman, *J. Am. Chem. Soc.*, **73**, 244 (1951).

(9) L. N. Owen, *J. Chem. Soc.*, 241 (1949).

trans-1-bromo-2-butene to equilibrate at room temperature. The mixture had a refractive index of n_D^{25} 1.4690. This refractive index indicated a mixture containing 46% 1-bromo-2-butene and 54% 3-bromo-1-butene.[10] The infrared spectrum of the mixture indicated the presence of only these two isomers.

1-Bromo-2-butene. 1-Bromo-2-butene (crotyl bromide) was purchased from Columbia Organic Chemicals, Inc., and used without further purification. n_D^{25} 1.4788. Lit.[10] n_D^{25} 1.4794.

Lithium aluminum hydride reductions. The lithium aluminum hydride reduction procedure was similar to that previously described.[5] Tetrahydrofuran was the solvent for both the halide and the hydride. After the addition of the lithium aluminum hydride at room temperature, the reaction mixture was refluxed (67°) for 1 hr. The reaction products distilled into a cold trap (dry-ice acetone) as formed and were weighed and analyzed by gas-liquid partition chromatography. In nearly every reaction the material balance was approximately 100%.

Anal. The chromatography equipment consisted of a 10 ft. by 1/4 in. copper tube containing dinonyl phthalate (30%) on 40–60 mesh fire brick (70%) as packing. The detector was a Gow-Mac thermal conductivity cell, helium was the carrier gas and the temperature was 30°. 3,4-Dichloro-1-butene: 100% *trans*-2-butene. 3-Chloro-1-butene: 5% *cis*-2-butene; 8% butadiene; 18% *trans*-2-butene; 69% 1-butene. 3-Bromo-1-butene (69%) and *trans*-1-bromo-2-butene: 26% *cis*-2-butene; 44% *trans*-2-butene; 30% 1-butene. 1,4-Dichloro-2-butene (purchased): 71% *cis*-2-butene; 29% *trans*-2-butene. 1,4-Dichloro-2-butene: (from butadiene): 100% *trans*-2-butene. *trans*-1-Chloro-2-butene: 100% *trans*-2-butene. *trans*-1-Bromo-2-butene: 100% *trans*-2-butene.

Acknowledgment. The authors wish to thank The Robert A. Welch Foundation for the financial support which made this research possible.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

---

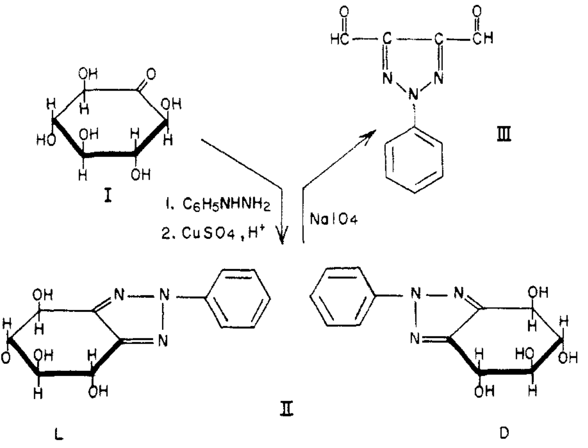
(10) M. S. Kharasch, E. T. Margolis and F. R. Mayo, *J. Org. Chem.*, 1, 393 (1936).

DL-1,2-Diketo-*myo*-inositol Phenylosotriazole and 2-Phenyl-2,1,3-triazole-4,5-dicarboxaldehyde

LAURENS ANDERSON AND JOHN N. ARONSON[1]

Received June 11, 1959

An interest in procedures for the carbon-by-carbon degradation of *myo*-inositol[2] prompted us to study osotriazole formation[3] with the racemic phenylosazone obtained by treating *myo*-inosose-2 (I) with excess phenylhydrazine.[4] Magasanik and Chargaff[5] had reported that they were unable to obtain the osotriazole from one of the optically active forms of this osazone, D(+)-1,2-diketo-*myo*-inositol bisphenylhydrazone. However, we found that the racemic osazone could be converted to the osotriazole II, albeit in poor yield, by the usual treatment with acidic copper sulfate. The osotriazole was degraded to the hitherto unknown 2-phenyl-2,1,3-triazole-4,5-dicarboxaldehyde (III).



EXPERIMENTAL[6]

DL-*1,2-Diketo-myo-inositol phenylosotriazole (II).* Thirteen g. of crude DL-1,2-diketo-*myo*-inositol bisphenylhydrazone[4] was refluxed for 2 hr. with 940 ml. of acidic copper sulfate solution (33 g. $CuSO_4 \cdot 5H_2O$ per liter of 0.01 *N* H_2SO_4) and 625 ml. of isopropanol.[7] The osazone gradually went into solution. After the solution had cooled, the copper was precipitated with hydrogen sulfide and removed by filtration, and the filtrate, after treatment with charcoal, was concentrated under vacuum to less than 200 ml. On standing 3 hr. at room temperature, the concentrate deposited 1.2 g. (12%) of light brown solid. Several recrystallizations of this from pyridine-benzene, pyridine-ether, and water gave colorless prisms melting at 278–282° (dec.). Losses of material in the recrystallizations were moderate.

Anal. Calcd. for $C_{12}H_{13}O_4N_3$ (263.35): C, 54.8; H, 5.0. Found: C, 53.8; H, 5.3.

Attempts to isolate additional quantities of the osotriazole by concentrating the reaction liquors were fruitless, as were efforts to improve the yield by varying the proportions of the reactants, and by using methanol, 2-methoxyethanol and acetone as solvents.

*Tetra-O-acetyl-*DL*-1,2-diketo-myo-inositol phenylosotriazole* was obtained by treating the free osotriazole with acetic anhydride and pyridine on the steam bath. After recrystallization from warm acetone, the tetraacetate melted at 194–195°.

---

[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

[2] The cyclitols mentioned in this note are named and numbered according to the system of H. G. Fletcher, Jr., L. Anderson, and H. A. Lardy, *J. Org. Chem.*, 16, 1238 (1951).

[3] E. G. V. Percival, *Advances in Carbohydrate Chem.*, 3, 37 (1948).

[4] H. E. Carter *et al.*, *J. Biol. Chem.*, 174, 415 (1948). The parent compound was called "*scyllo*-inosose" by these authors.

[5] B. Magasanik and E. Chargaff, *J. Biol. Chem.*, 174, 173 (1948).

[6] All crystalline compounds were recrystallized to constant melting point. Melting points were determined in capillary tubes. The thermometer used has been calibrated against Anschütz thermometers calibrated by the National Bureau of Standards. Microanalyses by the Micro-Tech Laboratories, Skokie, Illinois.