

refluxed on a water-bath for 21 hours. The ether was removed and the residue treated with water, filtered, dried and washed with ether twice. The ether-insoluble portion, m.p. 149°, is soluble in alcohol and gives a yellow color with ferric chloride; yield 95%.

*Anal.* Calcd. for C<sub>23</sub>H<sub>25</sub>O<sub>9</sub>Cl: C, 57.44; H, 5.24. Found: C, 57.62; H, 5.47.

5-(*p*-Acetoxyphenyl)-4,6-dicarbethoxy-2-(β-iodopropionyl)-cyclohexanedione-1,3 (I).—The procedure was similar to the above with the exception that to the dry sodio derivative and β-chloropropionyl chloride in dry ether two grams of dry potassium iodide was added and the mixture refluxed as described. The product melted at 145° and gave a yellow color with ferric chloride; yield almost quantitative. This compound was prepared first by Greenfield.<sup>8</sup>

*Anal.* Calcd. for C<sub>23</sub>H<sub>25</sub>O<sub>9</sub>I: C, 48.44; H, 4.45. Found: C, 48.95; H, 4.89.

5-(*p*-Acetoxyphenyl)-4,6-dicarbethoxy-2-(β-diethylamino-propionyl)-cyclohexanedione-1,3 (II).—5-(*p*-Acetoxyphenyl)-4,6-dicarbethoxy-2-(β-chloropropionyl)-cyclohexanedione-1,3 (4.8 g.) and 2.0 ml. diethylamine in dry ether were mixed, allowed to stand in ice-bath for 1 hour and then refluxed for 5 hours. The ether was removed and the residue was treated with chloroform. The undissolved part was washed with chloroform, then dissolved in a mixture of methyl alcohol and chloroform. The solution was filtered and to the cooled filtrate ether was added. A precipitate formed, m.p. 201–202°, yield 87%. The product gave a yellow color with the ferric chloride test.

*Anal.* Calcd. for C<sub>27</sub>H<sub>35</sub>O<sub>9</sub>N: C, 62.65; H, 6.81. Found: C, 62.37; H, 7.24.

5-(*p*-Hydroxyphenyl)-4,6-dicarboxy-2-(3-diethylamino-1-hydroxypropyl)-cyclohexanedione-1,3 (III).—Compound II was converted to III by the Meerwein-Ponndorf-Verley reduction. The procedure was similar to that described by Wilds.<sup>9</sup> In a 500-cc. round-bottomed flask were placed 4 g. of II (0.0076 mole), 3.5 g. of aluminum isopropoxide (0.0156 mole) and 250 ml. of dry isopropyl alcohol. A small fractionating column was attached to the flask with a water condenser set for distillation. After six hours of slow distillation, the distillate showed a negative acetone test. The remaining isopropyl alcohol was removed and the residue was dried under reduced pressure. Benzene was added to the residue to dissolve any unreacted aluminum isopropoxide. The residue was then treated with cold water and ammonium hydroxide was added to the mixture with mechanical stirring. After removal of the aluminum hydroxide, the filtrate was cooled, acidified with cold hydrochloric acid and allowed to stand in the refrigerator several hours. The precipitate which formed was collected, washed with distilled water, dried, and crystallized from alcohol. The first crop of crystals had m.p. 209° (IV).

*Anal.* Calcd. for C<sub>21</sub>H<sub>25</sub>O<sub>7</sub>N: C, 62.52; H, 6.23. Found: C, 62.72; H, 5.97.

Distilled water was added to the filtrate and the precipitate formed was dissolved in alcohol and reprecipitated with distilled water, collected and dried, m.p. 193° (III). It gave an orange color with ferric chloride.

*Anal.* Calcd. for C<sub>21</sub>H<sub>27</sub>O<sub>9</sub>N (III): C, 59.84; H, 6.46. Found: C, 60.06; H, 6.57.

(8) L. Greenfield, Creighton University M.S. Thesis, 1948.

(9) A. L. Wilds, "Organic Reactions," Editors Roger Adams, W. E. Bachmann, L. F. Fieser, J. R. Johnson, H. R. Snyder, Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 200–204.

DEPARTMENT OF CHEMISTRY  
CREIGHTON UNIVERSITY  
OMAHA, NEBRASKA

## A Synthesis of 1,3-Butylene Oxide

BY FRANZ SONDHEIMER<sup>1</sup> AND R. B. WOODWARD

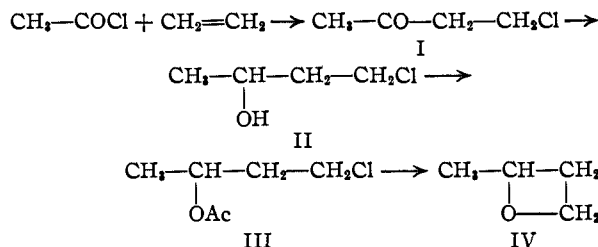
RECEIVED FEBRUARY 23, 1953

1,3-Butylene oxide (1,3-epoxybutane) (IV) was required for synthetic purposes. The previously

(1) Syntex, S. A., Laguna Mayran 413, Mexico, D. F.

described<sup>2</sup> method of preparation of this substance proceeded only in poor yield, and was not particularly suitable for laboratory scale production. For these reasons a convenient new synthesis of IV was developed.

The first step, the condensation of ethylene with acetyl chloride to give 4-chloro-2-butanone (I), has been described previously.<sup>3</sup> The use of excess acetyl chloride and the absence of solvent were recommended, and I was obtained in 40% yield. We have found that these precautions are unnecessary, and by applying the conditions used with propionyl chloride,<sup>4</sup> I could be isolated in 61% yield. The reduction of this chloroketone with lithium aluminum hydride proceeded smoothly to yield the corresponding alcohol II, which was acetylated to III.



The procedure for carrying out the last step, heating to 140° with ca. 90% aqueous potassium hydroxide, was based on that employed with the lower homolog, 3-chloropropyl acetate.<sup>5</sup> It seems however that the secondary nature of the acetoxy group in III favors this type of reaction, for a 66% yield of the required 1,3-butylene oxide (IV) was realized as compared with the 42–44% yield of 1,3-propylene oxide obtained from the above mentioned lower homolog containing a primary acetoxy group. The over-all yield in the present process is 30%.

### Experimental<sup>6</sup>

4-Chloro-2-butanone (I).—Acetyl chloride (510 g., 6.50 moles) was added during 20 minutes to a mixture of aluminum chloride (910 g., 6.82 moles) and chloroform (2 l.) with stirring and ice-salt cooling. At the end of the addition the temperature had risen to ca. 25°, and cooling was continued until it had fallen to 0°. Ethylene was then bubbled into the stirred mixture at such a rate that all was absorbed, the internal temperature being kept between 5 and 10° by continued ice-salt cooling. Gas started escaping after ca. 2 hours, and after another 30 minutes the reaction mixture was poured into a mixture of 1 l. of concentrated hydrochloric acid and 5 kg. of ice. The organic layer was washed with dilute hydrochloric acid, sodium bicarbonate and water, and was then dried and slowly evaporated through a 25-cm. Vigreux column. Distillation of the residue through the same column yielded the β-chloroketone I as a mobile liquid, b.p. 47° (16 mm.), *n*<sub>D</sub><sup>20</sup> 1.4299 (reported<sup>3</sup> b.p. 48° (15 mm.)). The yield was 421 g. (3.95 moles), or 61%.

4-Chloro-2-butanol (II).—The chloroketone (388 g.) in dry ether (400 cc.) was added during 1 hour to a stirred solution of 50 g. of lithium aluminum hydride in 1.5 l. of ether, so as to maintain gentle reflux. After stirring for another 30 minutes, water was added dropwise to decompose excess

(2) Celanese Corp. of America, British Patent 585,245 (C. A., 41, 4167 (1947)).

(3) *Inter al.*, J. R. Catch, D. F. Elliott, D. H. Hey and E. R. H. Jones, *J. Chem. Soc.*, 278 (1948).

(4) E. M. McMahon, J. N. Roper, W. P. Utermohlen, R. H. Hasek, R. C. Harris and J. H. Brandt, *THIS JOURNAL*, 70, 2971 (1948); R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *ibid.*, 74, 4223 (1952).

(5) C. R. Noller, *Org. Syntheses*, 29, 92 (1949).

(6) Boiling points are uncorrected.

reagent, then *ca.* 1.5 l. of 10% sulfuric acid was added and the aqueous layer was re-extracted several times with ether. The combined organic layers were washed with sodium carbonate solution and water, dried and evaporated through a 25-cm. Vigreux column. Distillation of the residue through the same column furnished 313 g. (79%) of the chlorocarbonyl, b.p. 67° (20 mm.),  $n_D^{20}$  1.4408 (this compound has previously been made by the reaction of  $\beta$ -chloropropionaldehyde with methylmagnesium iodide<sup>1</sup>; reported<sup>1a</sup> b.p. *ca.* 70° (13 mm.)). In addition a lower boiling fraction was obtained.

**4-Chloro-2-butyl Acetate (III).**—A solution of the chlorocarbonyl (300 g.) in 300 cc. of ether and 360 cc. of pyridine was cooled in ice and 330 g. of acetyl chloride was added dropwise during 90 minutes with stirring and continued cooling. Stirring was continued for 5 hours at room temperature and the mixture was then set aside overnight. Ice and ether were added, the organic layer was washed with water, dilute hydrochloric acid, sodium bicarbonate and water, dried and distilled through the Vigreux column. The acetate had b.p. 70° (16 mm.),  $n_D^{20}$  1.4260, and weighed 395 g. (95%).

**1,3-Butylene Oxide (IV).**—An apparatus as described by Noller<sup>2</sup> incorporating a 25-cm. Vigreux column (ref. 5, Note 2) was used and the receiver was cooled in ice-salt. A mixture of 437 g. of solid potassium hydroxide and 40 cc. of water was placed in the reaction flask, which was heated to 150° in an oil-bath, and a few cc. of the acetate was added. Thereupon the mixture became liquid, and stirring was commenced. The acetate (total of 389 g.) was then added dropwise with vigorous stirring at such a rate as to keep the inside temperature at 140–150°, and that at the distillation head at 70–85°. The reaction was quite exothermic and the inside temperature was maintained by keeping the oil-bath at 120–140°. The distillate passed over at a rate of *ca.* 1 drop/second. After 3 hours the addition was complete, and the oil-bath was heated to 160° for a further 30 minutes. The distillate (186.5 g.) was dried over 40 g. of solid potassium hydroxide, whereupon a lower aqueous layer separated. The upper layer was dried over a further 20 g. of potassium hydroxide, decanted and distilled through the 25-cm. Vigreux column. The fraction (134 g.) with b.p. 55–70° was refluxed with 15 g. of sodium hydride for 1 hour to remove impurities, and was then refractionated. The oxide was obtained as a pleasant smelling liquid, b.p. 60–61° (762 mm.),  $n_D^{20}$  1.3894, and weighed 122 g. (66%) (reported<sup>2</sup> b.p. 59.4–59.7° (736 mm.),  $n_D^{20}$  1.3889).

(7) (a) E. Fourneau and P. Ramart-Lucas, *Bull. soc. chim.*, [4] **25**, 364 (1919); (b) H. J. Backer and C. C. Bolt, *Rec. trav. chim.*, **54**, 68 (1935); (c) R. C. Elderfield, *et al.*, *THIS JOURNAL*, **68**, 1516 (1946).

CONVERSE MEMORIAL LABORATORY  
HARVARD UNIVERSITY  
CAMBRIDGE, MASS.

### The Reaction of Toluene Diisocyanate Dimer with Dibutylamine

BY J. H. SAUNDERS AND EDGAR E. HARDY

RECEIVED JULY 2, 1953

Isocyanate dimers are of interest principally because they may exhibit isocyanate activity only at elevated temperatures, and because they may occur as impurities in isocyanates, especially in polyisocyanates. The reactions of phenyl isocyanate dimer have been studied qualitatively, as by Hofmann,<sup>1</sup> and Bayer<sup>2</sup> has reported that the dimer of toluene diisocyanate (I) dissociates to the monomer at 150°. This dimer has been observed in this Laboratory to react with more than two equivalents of dibutylamine in refluxing toluene, in a modification of an analytical procedure for isocyanates.<sup>3</sup> To clarify further the chemistry of this dimer its

(1) A. W. Hofmann, *Ber.*, **4**, 246 (1871).

(2) O. Bayer, British Intelligence Objectives Subcommittee Final Report No. 719, July, 1946.

(3) S. Siggia and J. G. Hanna, *Anal. Chem.*, **20**, 1084 (1948).

reaction with di-*n*-butylamine in *o*-dichlorobenzene was studied briefly at 50–180°.

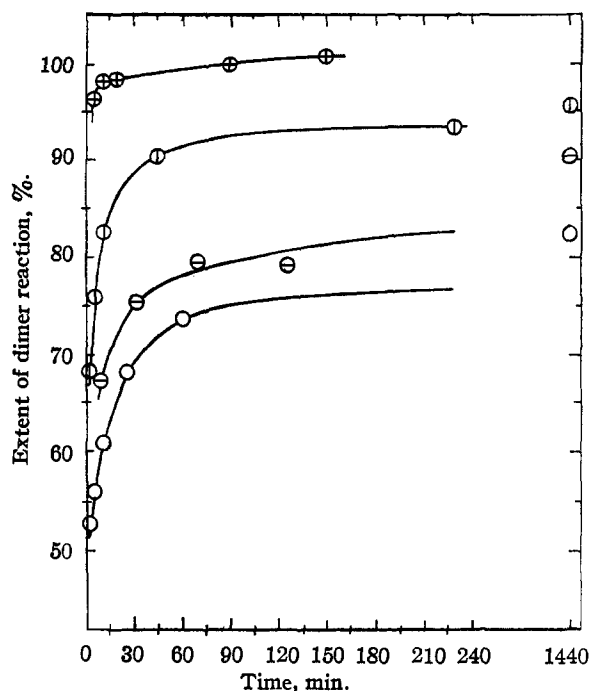
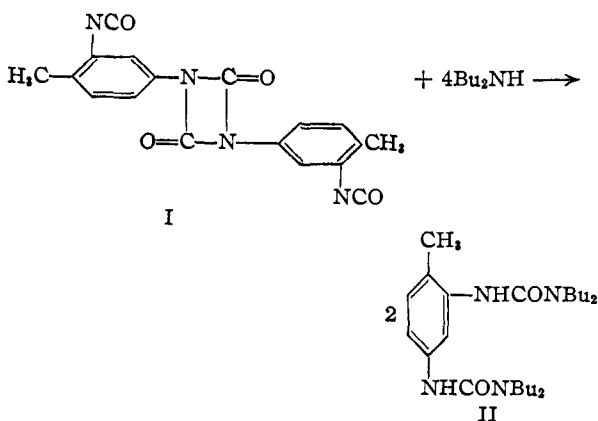


Fig. 1.—The reaction of toluene diisocyanate dimer with dibutylamine: O, reaction at 50°, 4:1 amine:dimer molar ratio; □, 70°, 4:1 ratio; ◇, 130°, 4:1 ratio; ⊕, 170–180°, 8:1 ratio.

The results are shown in Fig. 1. It is assumed that the first 50% of the reaction, which was very fast, corresponded to the reaction of the free isocyanate groups, and that further reaction took place at the dimerized groups. The dimer ring reacted at an appreciable rate, even at 50°, and reacted completely with 100% excess of amine in 1.5 hours at 170–180°. The reaction product gave an analysis in agreement with structure (II), and showed no depression of melting point with the reaction product from monomeric toluene diisocyanate and dibutylamine.



These results show that isocyanate polymers may exhibit considerable activity in the analysis for isocyanates, and that dimers will not be completely unreactive at moderate temperatures in systems containing amines. It is likely that dimers will