

(5 mm.). The crude distillate was recrystallized from methanol: yield, 10.5 g.; m. p. 71–72°.

Anal. Calcd. for $C_{12}H_8NO_2Br$: Br, 28.75. Found: Br, 29.12.

Summary

1. A study has been made of the oxidation products of the following polybromodiphenyls:

2,3'- and 3,4'-dibromodiphenyl, 2,3',5'-, 3,3',5'-, 3',4,5'-, 2,2',5'-, 2',3,5'-, 2',4,5'- and 2,4,6-tribromodiphenyls, and 2,4,4',6-tetrabromodiphenyl.

2. The preparation of those polybromodiphenyls not previously recorded is described.

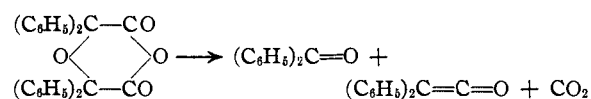
PHILADELPHIA, PENNA. RECEIVED SEPTEMBER 8, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

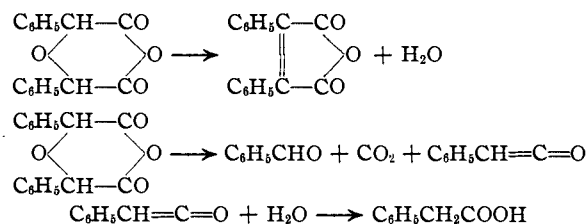
The Pyrolysis of Diglycolic Anhydride

BY CHARLES D. HURD AND HOWARD G. GLASS

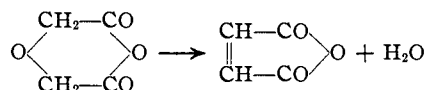
On pyrolysis, dibenzilic anhydride¹ yields benzophenone and diphenylketene. Dimandelic an-



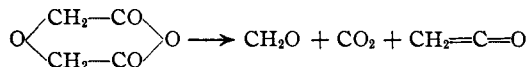
hydride² decomposes thermally at 250° into diphenylmaleic anhydride, phenylacetic acid, benzaldehyde, and oxides of carbon.



The present work deals with diglycolic anhydride. From the above one would predict for it a bidirectional breakdown on heating. One reaction should give rise to maleic anhydride



whereas the other should yield ketene



A good yield of maleic anhydride was obtained at 450–500°. Some ketene was observed too, but since water was formed in this reaction it must have changed much of the ketene into acetic acid.

The production of maleic anhydride from diglycolic anhydride involves lengthening of the carbon chain. This is an interesting, unusual method of bringing about such an effect.

(1) Staudinger, *Ber.*, **44**, 543 (1911).

(2) Hurd and Raterink, *THIS JOURNAL*, **55**, 1541 (1933).

Experimental

Diglycolic Anhydride.—To 35 g. of diglycolic acid was added 65 g. of acetic anhydride and the mixture was refluxed four hours. Then 35 g. of acetic acid was distilled off, 30 g. more of acetic anhydride added and the mixture was refluxed for two hours longer. On distillation 5 g. more of acetic acid was collected and 61 g. of acetic anhydride was recovered. The residue was vacuum distilled. There was collected 32 g. (94% yield) of diglycolic anhydride at 130° and 20 mm. It solidified on cooling; m. p. 94–95°. The derivative with aniline, diglycolic phenylimide, was prepared. Its melting point of 109–110° confirmed Anschutz' value³ of 111°.

Analysis of Mixtures of Maleic and Diglycolic Anhydrides.—The separation of these two anhydrides was accomplished satisfactorily by the selective solvent action of benzene. Both anhydrides were soluble in hot benzene whereas diglycolic anhydride separated on cooling the solution to 6°. After concentrating the filtrate and cooling till crystals of this compound no longer appeared, furan was added to the solution. After a time, crystals of the addition product of furan and maleic anhydride separated.⁴ This material melted at 122–124° and at 125° after recrystallization (literature, 125°).

In various mixtures, recovery of the diglycolic anhydride was almost quantitative and recovery of the maleic anhydride derivative was 89–95%. The results are presented in Table I.

TABLE I

SEPARATION OF MALEIC AND DIGLYCOLIC ANHYDRIDES

Mixture, g.		Diglycolic anhydride found	Maleic anhydride found	Maleic anhydride found	
Maleic anhydride	Di-glycolic anhydride			Furan deriv. G.	%
3.0	12.0	11.6	4.75	94	
1.0	1.0	1.0	1.6	95	
0.8	1.0	0.97	1.25	93	
.6	1.0	.95	0.90	89	
.4	1.0	.96	.60	89	
.2	1.0	.97	.30	89	

Pyrolysis of Diglycolic Anhydride.—The sample of diglycolic anhydride was placed in a test-tube with a side

(3) Anschutz, *Ann.*, **273**, 66 (1892).

(4) Diels and Alder, *Ber.*, **62**, 554 (1929).

arm capillary. An oil-bath at 100° kept the anhydride melted and mercury, which was dropped in through a capillary jet, forced the anhydride at a uniform rate into the top of the vertical hot reaction tube. The reaction products were condensed in a side-arm flask, attached to the bottom of the tube. The flask was cooled in ice and connected to a gas collecting bottle. The tube was flushed out with nitrogen before each run.

The effective hot volume of the reaction tube was 87 cc. This volume makes allowance for the volume of the thermocouple well. The tube was electrically heated in a furnace whose temperature was recorded and controlled by a Leeds and Northrup potentiometer-type recorder-controller.

In the first run at 450°, 20 g. of diglycolic anhydride was passed through the tube during eighty minutes (contact time, about forty seconds). From the reaction products was obtained 15.5 g. of diglycolic anhydride and 1.2 g. of diglycolic acid. Hence, 3.3 g. of the anhydride was the amount pyrolyzed. The furan derivative weighed 3.2 g. From Table I it may be assumed that this represents 95% of the maleic anhydride present. Hence, the corrected yield of maleic anhydride, based on the diglycolic anhydride not recovered, was 71%.

The second run was performed also with 20 g. of diglycolic anhydride during eighty-seven minutes (contact time, forty-two seconds). There was recovered 10.2 g. of the anhydride and 1.5 g. of diglycolic acid; therefore, 8.3 g. of

the anhydride was pyrolyzed. The furan derivative weighed 4.9 g. With the 95% correction factor, this represents a 44% yield of maleic anhydride.

The gas evolved in runs 1 and 2, respectively, measured 600 and 2500 cc. The gas was analyzed for CO₂, unsaturates, H₂ and CO. These relative amounts were formed in run 1 (% by volume): 16.6, 4.7, 20.7, 58.0. In run 2: 13.1, 21.6, 20.7, 44.6.

Ketene in the Products.—An 8-g. sample of diglycolic anhydride was pyrolyzed in the same apparatus at 500°. The gases which were evolved were passed through a low-pitched coil condenser cooled to -15° by ice and salt, and the uncondensed gas was conducted through standard alkali. The ketene in the gas stream neutralized 0.56 cc. of 2.218 *N* sodium hydroxide. This represents 0.00124 mole of ketene or 0.052 g. This is a 4% yield, calculated on the basis of 3.3 g. of unrecovered diglycolic anhydride.

Summary

Diglycolic anhydride undergoes pyrolysis at 450–500° into maleic anhydride. This reaction involves lengthening of the carbon chain. Concurrently, a small yield of ketene is obtained. A method for the separation of mixtures of diglycolic anhydride and maleic anhydride is included.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUW UNIVERSITY]

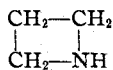
Azetidine Derivatives. I. 2,4-Diketo-3-hydroxy-3-arylazetidines

By J. L. RIEBSOMER, HOWARD BURKETT, THOMAS HODGSON AND FRED SENOUR

The five- and six-membered heterocyclic compounds are well known since they are found in such important substances as pyrrole and pyridine. Interest in the structure and synthesis of such compounds has been fostered by the study of natural products in which these basic structures are often found.

On the other hand, four-membered heterocyclic compounds containing nitrogen in the ring have been found difficult to prepare and since no relationship between their structure and important natural products has been observed, this field of chemistry has been almost neglected.

Azetidine, or trimethyleneimine, has been known since about 1890¹ when it was prepared by the distillation of trimethylenediamine hydrochloride and by heating γ -bromopropylamine with alkali.²



A few syntheses of substituted azetidines have

- (1) Ladenburg and Sieber, *Ber.*, **23**, 2727 (1890).
 (2) Gabriel and Weiner, *ibid.*, **21**, 2875 (1888).

been reported such as the synthesis of 3,3-dimethylazetidine,³ *N*-phenyl-3,3-diphenyl-2,4-diketo-azetidine,⁴ *O*-methylol-*O*-benzyleneimine,⁵ 3-hydroxy-3-2,4,6-trimethoxyphenyl-2,4-diketo-azetidine,⁶ and others.^{7,8,9,10}

The purpose of this paper is to present a new method for the synthesis of substituted diketo-azetidines and to report certain pharmacological studies of these new compounds.

In an attempt to condense phenylhydroxymalonic esters¹¹ with urea in the presence of sodium ethylate to produce the corresponding barbituric acid derivatives, there were produced instead imides or azetidine derivatives such as

- (3) Komppa and Sevón, *Ann. Acad. Sci. Fennicae*, **37A**, 7, 8 (1933).
 (4) Staudinger, Göhring and Schöller, *Ber.*, **47**, 46 (1914); Staudinger and Becker, *ibid.*, **50**, 1016 (1917).
 (5) Orlov, *Chem. Zentr.*, **76**, 674 (1905); **77**, 1413 (1906).
 (6) Szeki, *Ber.*, **56**, 2464 (1923).
 (7) Gibbs and Marvel, *THIS JOURNAL*, **56**, 725 (1934); *ibid.*, **57**, 1137 (1935).
 (8) Govaert, *Proc. Acad. Sci. Amsterdam*, **37**, 156 (1934).
 (9) LeFèvre, *J. Chem. Soc.*, **733** (1929).
 (10) Warren and Briggs, *Ber.*, **64B**, 26 (1931).
 (11) Riebsomer, Irvine and Andrews, *THIS JOURNAL*, **60**, 1015 (1938).