(phenol coefficient 156), that upon *Eberthella paradysenteriae* with the hexyl derivative (phenol coefficient 333), and decreases thereafter. The other four test organisms, in spite of their genetic and morphological differences, show a remarkable parallelism in a qualitative and a quantitative respect in their behavior toward the substances studied. With reference to these organisms the maximum germicidal potency is reached by derivatives of higher molecular weight, *viz.*, the *n*-octyl derivative in the case of *Staphylococcus aureus* (phenol coefficient 1750), and the *n*-heptyl derivative in the case of the remaining three organisms (phenol coefficients: for *Streptococcus* 2220, for *Mycobacterium smegmatis* 1250, for *Trichophyton rosaceum* 667). The germicidal action of the isomeric derivatives with the same number of carbon atoms, but in branched chains, in alicyclic groups or distributed over several radicals, is lower in comparison.

The results thus far obtained appear to be sufficiently significant to suggest an extension of the work outlined into the field of chemotherapy.

BLOOMFIELD, NEW JERSEY

RECEIVED JANUARY 10, 1933
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Preparation and Pyrolysis of Dibenzyl Ketone, Phenylacetic Anhydride and Diphenylacetic Anhydride

BY CHARLES D. HURD, ROBERT CHRIST AND CHARLES L. THOMAS

Phenylacetic anhydride was synthesized by the general method of refluxing the acid with acetic anhydride, a method which was also found to give excellent results in the synthesis of diphenylacetic anhydride. Phenylacetic anhydride, but not diphenylacetic anhydride, underwent pyrolysis on vacuum distillation. At sufficiently high temperatures (275°), the latter gave rise to diphenylacetic acid in high yields and to diphenylmethane and tetraphenylethylene in lesser yields.

Staudinger[1] obtained diphenylacetic anhydride from dimethylmalonic diphenylacetic anhydride, $(CH_3)_2C(CO—O—COCH(C_6H_5)_2)_2$, by vacuum distillation and suggested that it decomposed in turn if the bath temperature reached 200–220°, since some diphenylketene then distilled over (20 mm.). In the present work, an initial decomposition temperature of 275° was found and no diphenylketene was isolated as such. Hence, the diphenylketene in Staudinger's work probably came directly from the mixed anhydride.

Phenylacetic anhydride proved interesting to study for it gave good yields of dibenzyl ketone[2] by distillation at reduced pressure. This work

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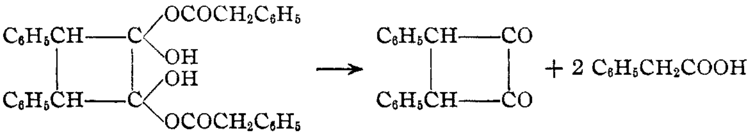
[1] Staudinger, Anthes and Schneider, *Ber.*, **46**, 3539 (1913).

[2] Previously this has been prepared by the dry distillation of calcium or barium phenylacetates: Pohow, *Ber.*, **6**, 560 (1873); Apitzsch, *ibid.*, **37**, 1429 (1904); Stobbe, Russwurm and Schulz, *Ann.*, **308**, 175 (1899).

suggests that Bakunin and Fisceman's[3] unidentified solid (m. p. 35°; anal., C, 87; H, 7) was dibenzyl ketone. It was isolated with phenylacetic anhydride when the reaction product of acetic anhydride and sodium phenylacetate was vacuum distilled.

In the present work some phenylacetic acid was admixed with the dibenzyl ketone but it was easily removed. There was also considerable non-volatile residue. The latter was not investigated because of Kalnin's[4] article which appeared during the progress of this work. Using a technique which seemed almost identical to ours (he distilled phenylacetic anhydride to 240° (30 mm.) whereas ours was to 210° (14 mm.)), Kalnin reported a distillate of phenylacetic acid but made no mention of dibenzyl ketone. The non-volatile, red residue was shown to contain diphenylcyclobutane-α-dione or phenylketene dimer. Instead of considering it to be formed *via* phenylketene, Kalnin regarded it as a pyrolytic product of an unsymmetrical dimer of enolic phenylacetic anhydride



Presumably our residue was similar to Kalnin's. Why our distillate differed from his is not evident.

Dibenzyl Ketone.—Were this substance to pyrolyze like acetone, the anticipated products would be toluene and phenylketene, analogous to methane and ketene. Actually, at 500–700° good yields of toluene were realized. Phenylketene may have been the precursor of carbon monoxide, anthracene and polymerized material but none was found as such.

Rice's mechanism of pyrolysis[5] is applicable to dibenzyl ketone and to acid anhydrides.[6] It postulates preliminary scission into radicals; *e. g.*, $C_6H_5CH_2$— and $C_6H_5CH_2CO$— from dibenzyl ketone, or $(C_6H_5)_2CHCOO$— and $(C_6H_5)_2CHCO$— from diphenylacetic anhydride. The $C_6H_5CH_2CO$— or $(C_6H_5)_2CHCO$— radicals decompose into H— and a ketene which may decompose further. The H—, $C_6H_5CH_2$— or $(C_6H_5)_2CHCOO$— radicals hydrogenate themselves to H_2, $C_6H_5CH_3$ or $(C_6H_5)_2CHCOOH$ at the expense of neighboring undecomposed ketone or anhydride molecules giving, respectively, $C_6H_5CH_2CO\underset{|}{C}HC_6H_5$ and $(C_6H_5)_2CHCOOCO\underset{|}{C}(C_6H_5)_2$ which readjust themselves into the ketenes or their decomposition products and radicals ($C_6H_5CH_2$— and $(C_6H_5)_2CHCOO$—) which continue the cycle.

Mention may be made of the secondary decompositions. With mild

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[3] Bakunin and Fisceman, *Gazz. chim. ital.*, **46**, I, 77 (1916).

[4] Kalnin, *Acta Univ. Latviensis, Kim. Fakultates Serija* **1**, No. 17, 455 (1930).

[5] Rice, THIS JOURNAL, **53**, 1959 (1931); *Chem. Reviews*, **10**, 147 (1932).

[6] Regarding acetic anhydride, see Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907); Deakin and Wilsmore, *ibid.*, **97**, 1968 (1910); Peytral, *Bull. soc. chim.*, **35**, 969 (1924); Bamberger, *Ber.*, **43**, 3517 (1910).

high temperature conditions the ketenes may polymerize, but with more rigorous conditions decomposition into carbon monoxide and a bivalent radical must occur. The latter may appropriate hydrogen atoms (*e. g.*, $C_6H_5CH< \longrightarrow C_6H_5CH_3$; etc.) from adjacent molecules or undergo building-up processes (*e. g.*, $(C_6H_5)_2C<$ to $(C_6H_5)_2C=(C_6H_5)_2$; $C_6H_5CH<$ to anthracene, etc.). The acids may undergo decarboxylation or, as in the case of phenylacetic anhydride and acetic anhydride, they may change into the ketone. In confirmation, phenylacetic *acid* is known[7] to generate dibenzyl ketone by heating in a sealed tube.

Experimental Part

Diphenylacetic Anhydride.—Fifty grams each of diphenylacetic acid and acetic anhydride were refluxed for two hours and then the excess of acetic anhydride was distilled off. The residue was a thick, brown liquid which crystallized suddenly when treated with a little ether. The ether absorbed most of the color. The yield was 43–44 g. (90–92%). It distilled undecomposed at 182° and 3 mm. It melted[8] at 98°.

Phenylacetic anhydride was made similarly.[9]

Synthesis of Dibenzyl Ketone.—A mixture of 100 g. each of phenylacetic acid and acetic anhydride was refluxed two hours and then distilled till the temperature of the liquid reached 200°. The residual phenylacetic anhydride was then heated *in vacuo*. Between 165–210° (14 mm.), 62–70 g. of crude dibenzyl ketone distilled which solidified on cooling. The residue (18 g.) was a viscous mass which solidified as it cooled.

The phenylacetic acid present in the crude ketone was extracted with warm dilute sodium hydroxide. The insoluble dibenzyl ketone melted at 30° with no further purification; yield, 37–47 g., or 48–61% based on the total phenylacetic acid. Its phenylhydrazone melted at 126–127°.

The presence of a small amount of sodium acetate did not influence the yield. From an experiment with 50 g. of phenylacetic acid, 50 g. of acetic anhydride and 1 g. of sodium acetate there was isolated 22.6 g. (58%) of dibenzyl ketone.

When pure phenylacetic anhydride (28 g.) was heated in a Claisen distilling flask at a lower temperature, so that the escaping vapors did not exceed 150°, there was collected eventually about 6 cc. of toluene, which probably came by the way of phenylacetic acid.

Pyrolysis of Dibenzyl Ketone.—Drops of the ketone (liquid) were forced by mercury displacement into the top of a vertical glass tube (0.8 × 100 cm., the heated portion being 75 cm.) which was surrounded by a controlled electric furnace. Five-cc. samples were taken for each run.

The effluent vapors were passed directly into 5 cc. of cold aniline to test for phenylketene and to condense other liquid products. From there, the gases were collected. In five experiments at 500, 550, 600, 650 and 700° the contact times, respectively, were 12, 11.6, 11.6, 6.6 and 6.8 sec. (actual duration, 8, 8.2, 8.7, 5.2, 5.7 minutes) and the volume of gas formed was 0, 20, 85, 395 and 500 cc. The analysis of the gas from the 650–700° experiments was: CO, 83.5% by vol.; H_2, 8.8; CO_2, 1.0; unsaturates, 1.0; saturates (n in $C_nH_{2n+2} = 2.16$), 5.4.

No phenylacetanilide was obtained from the aniline solution but there was found toluene and unchanged ketone. More toluene and less ketone came in the experiments

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[7] Engler and Löw, *Ber.*, **26**, 1436 (1893).

[8] Staudinger, *ibid.*, **38**, 1738 (1905). Note, however, that in *Ann.*, **356**, 79 (1907), Staudinger gives 91.5–92° as the melting point.

[9] Autenrieth and Thomae, *Ber.*, **57**, 424 (1924).

at the higher temperatures. The residue (1–2 g.) after distilling to 210° (15 mm.) was dissolved in ether. The Schiff base (between aniline and dibenzyl ketone) was precipitated by dry hydrogen chloride, filtered off, and the ether solution evaporated. The residue was mixed with petroleum ether, which dissolved gummy material containing some dibenzyl ketone which was attested by its phenylhydrazone (m. p. 119°), and left crystals of anthracene. The latter melted at 195° and gave a mixed m. p. of 196–197° with anthracene melting at 205°. The quantity of anthracene was too small to purify by crystallization.

Pyrolysis of Diphenylacetic Anhydride

Flow Method.—The same technique was used as with dibenzyl ketone. Slight decomposition occurred at 500°. Most of the original anhydride was recoverable. In three experiments with 3-g. samples, 40, 60 and 140 cc. of gas (CO_2:CO = 5:3) were liberated when the hot contact times were adjusted to 26, 60 and 156 seconds, respectively. Likewise, at 600°, 160 and 400 cc. of gas resulted with contact times of 22 and 113 sec. At 700°, 105 and 200 cc. were produced with the brief contact times of 0.14 and 0.80 sec. The products of the 600 and 700° experiments contained diphenylmethane but no tetraphenylacetone or 9,10-diphenylanthracene (compare anthracene from phenylacetic anhydride).

Static Method.—Twenty grams of diphenylacetic anhydride was placed in a Claisen flask and heated gradually to 270°, at which temperature gas evolution became appreciable. The heating was continued for two and one-half hours between 270–285°. There was evolved 0.433 g. of carbon dioxide (absorbed in ascarite). In another similar experiment it was found that the ratio of CO_2 to CO was about 1:2. The residue in the flask was then distilled at 4 mm.: b. p. 70–80°, 2.2 g. of diphenylmethane; to about 170°, 12.1 g. of diphenylacetic acid; 5.5 g. of brown residue from which was extracted 2 g. of tetraphenylethylene by crystallization from water–acetone.

Identification of the Compounds Formed.—The diphenylmethane melted at 26°. Oxidation by potassium dichromate in acetic acid converted it to benzophenone whose oxime melted at 140°. The diphenylacetic acid melted at 145° after one crystallization from ether and it was soluble in dilute sodium hydroxide. Tetraphenylethylene was synthesized for comparison by refluxing diphenylmethane and diphenyldichloromethane (from $(C_6H_5)_2CO + PCl_5$) for six hours and then crystallized from methanol; m. p. 219°. Tetraphenylethylene from the pyrolysis melted at 221°; mixed m. p. 219.5°.

Summary

Phenylacetic and diphenylacetic anhydrides were synthesized from the corresponding acids by heating with acetic anhydride. Dibenzyl ketone was synthesized by pyrolysis of phenylacetic anhydride, evidently *via* phenylacetic acid because diphenylacetic anhydride pyrolyzed smoothly into diphenylacetic acid. Several anomalies in the literature are pointed out. Toluene was the chief pyrolytic product from dibenzyl ketone. These pyrolyses may be interpreted satisfactorily by assuming initial scission into radicals.

EVANSTON, ILLINOIS

RECEIVED JANUARY 13, 1933
PUBLISHED JUNE 6, 1933