4.5 liters of dry benzene, 260 g. (2 moles) of acetoacetic ester and 46 g. (2 moles) of sodium. The mixture was stirred and allowed to reflux gently for twenty-four hours. The solution was then cooled slightly and 350 g. (2.5 moles) of benzoyl chloride added slowly over a period of three hours. The mixture was refluxed with stirring for eight hours. It was then cooled to room temperature and 500 g. of cracked ice added. After shaking thoroughly the benzene layer, which contains the benzoylacetoacetic ester, was separated and the benzene distilled. The residue was then distilled from a Claisen flask with modified side-arm and the fraction boiling at 177–181° at 20 mm. collected; yield, 350 g. or 74.8% of the theoretical.

Hydrolysis of Benzoylacetoacetic Ester.—The first hydrolysis recorded in Table I was made according to Claisen's directions.[4] The remaining hydrolyses were made in accordance with the procedure outlined below, the only variables being the amounts of ammonia and ammonium chloride. The amounts stated in the following procedure are those of Run 5 which represents the optimum conditions.

Thirty-two grams (0.6 mole) of ammonium chloride was dissolved in 150 cc. (8.3 moles) of water and 10 cc. (0.10 mole) of ammonia (sp. gr. 0.9) added. The solution was warmed to 40° and 58.5 g. (0.25 mole) of benzoylacetoacetic ester added. The solution was kept at 40° for ten minutes and then cooled rapidly by placing the flask in an ice-bath. It was extracted twice with 100 cc. of ether and the ether solution dried with anhydrous magnesium sulfate. The ether was distilled and the residue distilled *in vacuo;* yield, 37.5 g. (78.1% of the theoretical) of benzoylacetic ester boiling at 165–169° at 20 mm.; sp. gr. at 20°, 1.1098; n_D^{20} 1.5498.

Summary

The preparation and partial hydrolysis of benzoylacetoacetic ester to give benzoylacetic ester have been studied and optimum conditions worked out.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF AMINES.
V. DERIVATIVES OF TERTIARY AMINES

BY C. S. MARVEL, E. W. SCOTT AND K. L. AMSTUTZ

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Solid derivatives of tertiary amines suitable for identification purposes are not always available. The methiodides, picrates, chloroplatinates, chloro-aurates and simpler salts such as the hydrochlorides, hydrobromides, etc., are at times useful but no one derivative is generally applicable to a wide number of amines. These derivatives have the common fault of melting with some decomposition and the temperature of decomposition is usually dependent on the rate of heating.

The most characteristic reaction of tertiary amines is the formation of quaternary ammonium compounds by addition to the nitrogen atom. It is generally true that the greater the proportion of the hydrocarbon part of the molecule in a quaternary ammonium salt, the more likely the compound is to have a sharp melting point. With this idea in mind, the addition of benzyl chloride, *p*-nitrobenzyl chloride and phenacyl chloride to a large number of tertiary amines was tried. The results were disappointing. Benzyl chloride reacted with four common amines to give new derivatives which were easily prepared and crystallized, but many products were too difficult to purify. *p*-Nitrobenzyl chloride was not at all satisfactory. Phenacyl chloride reacted with pyridine and α-picoline to give quaternary ammonium salts melting at 113 and 157°, respectively, but did not seem to show promise of general usefulness.

Several cases of the formation of quaternary ammonium compounds from tertiary amines and esters of arylsulfonic acids have been reported. A patent[1] describes the addition products of several quinoline derivatives with methyl and ethyl *p*-toluenesulfonates, and ethyl *p*-bromotoluenesulfonates. The melting points of these derivatives were reported as follows: 1-ethyl-2-methylquinolinium *p*-toluenesulfonate, 105°; 1-ethyl-2,6-dimethylquinolinium *p*-toluenesulfonate, 120°; 1,2-dimethylquinolinium *p*-toluenesulfonate, 134°; 1-ethyl-2-methylquinolinium *p*-bromotoluenesulfonate, 142°. More recently Simon and Frerejacques[2] observed that the methyl esters of several complex arylsulfonic acids combined with hexamethylenetetramine and some other complex tertiary amines to give products with sharp melting points. Rodionow[3] has described trimethylphenylammonium benzenesulfonate, m. p. 180–181°; dimethylethylphenylammonium *p*-toluenesulfonate, m. p. 48–49°; trimethylphenylammonium *p*-toluenesulfonate, m. p. 160–161°, and the methyl *p*-toluenesulfonate derivatives of several alkaloids.

The properties of these addition products suggested that methyl *p*-toluenesulfonate might prove to be a general reagent for use in identifying tertiary amines. A number of compounds of this type have been prepared and characterized. The reagent was found to be particularly useful with ring nitrogen compounds. Practically all of the pyridine and quinoline derivatives which were prepared, were well suited for identification purposes. However, it is less useful for the other types of amines studied as too many derivatives failed to crystallize.

Other experiments were made in the use of methyl *p*-bromobenzenesulfonate and methyl methanesulfonate. Each of these reagents gave some crystalline derivatives but none was useful where the methyl *p*-toluenesulfonate was unavailable.

Experimental Part

The addition compounds which are described in the tables were all prepared by mixing 1 g. of the amine and 2 to 3 g. of the reagent (benzyl

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[1] German Patent 170,048, *Chem. Zentr.*, I, 1857 (1906).

[2] Simon and Frerejacques, *Compt. rend.*, **178**, 945 (1924).

[3] Rodionow, *Bull. soc. chim.*, [4] **39**, 305 (1926).

chloride, methyl *p*-toluenesulfonate, methyl *p*-bromobenzenesulfonate or methyl methanesulfonate) in 10 cc. of dry benzene. The mixture was heated to boiling for about thirty minutes, cooled and filtered. The product was recrystallized by dissolving in the least amount of boiling ethyl alcohol and adding ethyl acetate until the material began to precipitate. The melting points given in the table were taken on compounds which had been purified to constant melting point.

TABLE I

NEW DERIVATIVES OF TERTIARY AMINES WITH BENZYL CHLORIDE

Amine	M. p., °C.	Cl calcd., %	Cl found, %
Diethylaniline	104	12.86	12.68
Dimethyl *p*-toluidine	171	13.60	13.04
6-Methylquinoline	209	13.15	13.04
Tri-*n*-butylamine	185	11.33	11.45

TABLE II

NEW DERIVATIVES OF TERTIARY AMINES AND SULFONIC ESTERS

Amine	Reagent, methyl ( )-sulfonate	M. p., °C.	S calcd., %	S found, %
Pyridine	*p*-Toluene	138–139	12.08	11.93
α-Picoline	*p*-Toluene	149–150	11.45	11.31
α-Chloropyridine	*p*-Toluene	119–120	10.68	10.78
Quinoline	*p*-Toluene	125–126	10.15	9.98
2-Methylquinoline	*p*-Toluene	161[a]	9.73	9.48
6-Methylquinoline	*p*-Toluene	153–154	9.73	9.87
6-Chloroquinoline	*p*-Toluene	142–143	9.10	9.21
6-Bromoquinoline	*p*-Toluene	150–152[b]	8.12	8.12
2,6-Dimethylquinoline	*p*-Toluene	175	9.32	9.54
Isoquinoline	*p*-Toluene	163	10.15	10.05
Dimethylaniline	*p*-Toluene	161[c]	....	...
Dimethyl-*p*-toluidine	*p*-Toluene	85	9.98	10.21
Di-*n*-butylaniline	*p*-Toluene	180	8.19	7.98
Tri-*n*-amylamine	*p*-Toluene	76–80[d]	7.75	8.16
Dimethylaniline	*p*-Bromobenzene	218–220	8.60	8.23
Dimethylaniline	Methane	192° (dec.)	13.85	14.00

[a] This melting point is higher than that recorded in the patent literature (Ref. 1). [b] This product seemed to soften somewhat at 95°. [c] Ref. 3. [d] The amount available was not great enough to permit crystallization to constant melting point.

Methyl *p*-toluenesulfonate gave oily products with the following amines: diethylaniline, di-*n*-propylaniline, di-*iso*propylaniline, ethylbenzylaniline, diethylallylamine, di-*n*-butylallylamine and nicotine.

Summary

1. Benzyl chloride, *p*-nitrobenzyl chloride, phenacyl chloride, methyl *p*-toluenesulfonate, methyl *p*-bromobenzenesulfonate and methyl methanesulfonate have been investigated as reagents for use in the preparation of derivatives for the identification of common tertiary amines.

2. Methyl *p*-toluenesulfonate has been found to be a fairly general reagent and to be particularly useful in the case of ring nitrogen compounds.

URBANA, ILLINOIS

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXIV. RING MIGRATION IN THE GLYCEROL CYCLIC ACETALS. BEHAVIOR OF PARA-NITROBENZYLIDENE GLYCEROL[1]

BY HAROLD HIBBERT, MURIEL E. PLATT AND NEAL M. CARTER

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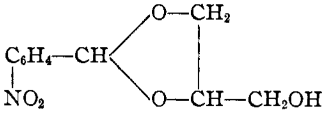
The close structural relationships existing between cyclic acetals on the one hand and carbohydrates, anhydro sugars and polysaccharides on the other has been emphasized frequently in this series of communications.[2] The present investigation deals with the interconversion of the 5- and 6-membered *p*-nitrobenzylidene glycerols



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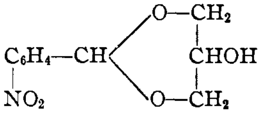

B

It has been found, in accordance with previous work carried out on the benzylidene and methylidene glycerols,[3,4] that in the presence of a trace of dry hydrochloric acid gas the six-membered derivative (B) is readily converted into an equilibrium mixture of the five- and six-membered isomers. By carrying out the reaction at 100° for one and a half hours, an equilibrium is apparently reached in which the proportion of 6:5-membered acetals is represented by 1:2.

In a second series of experiments, carried out by heating the crystalline six-membered acetal (B) with dilute hydrochloric acid ($N/10$) in a sealed tube at 100° for varying lengths of time, it was found that after about an hour an equilibrium mixture was obtained in which the six- and five-membered rings were present in the ratio of 0.37:1. In this series of experiments certain discrepancies came to light in that, for example, discordant results were obtained if the crystalline 6-membered acetal recovered

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[1] Constructed from the thesis of Muriel E. Platt as presented to the Graduate School of McGill University in June, 1929, in candidacy for the degree of Master of Science.

[2] Hibbert and co-workers, THIS JOURNAL, **45**, 734 (1923); **50**, 2235, 2242 (1928); **51**, 620 (1929).

[3] Hibbert, Whelen and Hill, *ibid.*, **50**, 2235 (1928).

[4] Hibbert and Carter, *ibid.*, **50**, 3120 (1928).