Barbier–Wieland Degradation of VIb to *trans*-2-Phenylcyclohexaneacetic Acid (IIIb).—A 0.500-g. sample of *trans*-β-(2-phenylcyclohexane)-propionic acid (m. p. 78–82°) was subjected to the Barbier–Wieland degradation under previously described[14] conditions except that the time of refluxing with acetic anhydride was increased to two and one-half hours. The crude product (IIIb) consisted of 0.110 g. (23%) of a white powder, m. p. 110–114° (previous softening). Recrystallization from hexane gave colorless plates, m. p. 113.5–114.5°, showing no depression in m. p. when admixed with an authentic sample of *trans*-2-phenylcyclohexaneacetic acid.

Summary

The configurations of the *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids and the *cis*- and *trans*-β-(2-phenylcyclohexane)-propionic acids have been proved by relating these acids, *via* the Arndt–Eistert homologation and the Barbier–Wieland degradation, to the configurationally established *cis*- and *trans*-2-phenylcyclohexaneacetic acids.

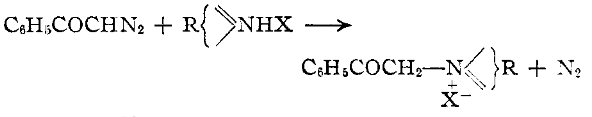
ST. LOUIS, MISSOURI RECEIVED JUNE 10, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Diazoketones with Heterocyclic Amine Salts

BY L. CARROLL KING AND F. M. MILLER

It has been found that diazoketones react with salts of certain heterocyclic amines to yield the corresponding quaternary salts.[1] Using diazoacetophenone, the reaction may be formulated as



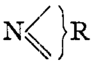
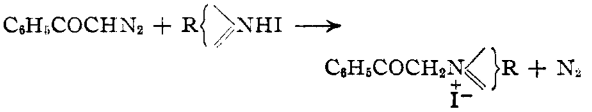
where  represents any of the heterocyclic bases listed in Table I, and X^- may be the anion of hydrochloric, hydrobromic, hydriodic, phosphoric, sulfuric, perchloric or *p*-toluenesulfonic acid.

TABLE I



		Yield,[a]	M. p., °C.[b]	
Compound		%	Found	Reported
1-Phenacyl-2-picolinium	iodide	27	203–205	200–202[c]
	perchlorate[e]		183–188	185–189[c]
1-Phenacylquinolinium	iodide	21	185–188	187–192[c]
	perchlorate[e]		191–193	193–195[c]
2-Phenacylisoquinolinium	iodide	68	176–177	178–180[c]
	perchlorate[e]		189–192	194–197[c]
2-Phenacyl-3-methylisoquinolinium	iodide	60	196–198	199–199.7[d]
	perchlorate[e]		191–193	193–195

[a] Based on the diazoketone. These preparations were carried out by method (b) (see experimental part). [b] All melting points were observed on a Fisher–Johns melting point block. [c] These compounds were compared with authentic material previously prepared in this Laboratory, King and McWhirter, THIS JOURNAL, **68**, 717 (1946). [d] Hartwell and Kornberg, *ibid.*, **68**, 868 (1946). [e] Prepared by adding perchloric acid to the iodide in dilute alcohol solution.

The generality of this method was established by allowing diazoacetophenone to react with the hydriodide salts of a number of heterocyclic bases, Table I, and with a number of acid salts of pyridine, Table II. In all cases the expected quaternary salt was obtained and the yield of it compared favorably with the yield of the substance as prepared by other methods.[1] The yield obtained from the perchloric acid salt of pyridine was particularly good.

TABLE II[a]

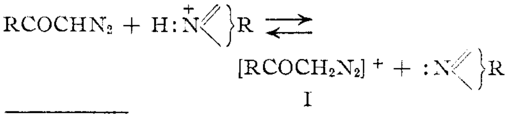
$$C_6H_5COCH_2N + C_5H_5NHX \longrightarrow \underset{X^-}{C_6H_5COCH_2\overset{+}{N}C_5H_5} + N_2$$

	Yield, %,[b] of 1-phenacylpyridinium salt		
X^-	Method a[c]	Method b[c]	Method c[c]
Iodide	66[d]	70[d]	65[d]
Chloride	74[e]	84[e]	70[e]
Bromide	73[e]	86[e]	74[e]
Sulfate	14[e]	19[e]	15[e]
Phosphate	15[e]	22[e]	14[e]
Tosylate	60[e]	71[e]	63[e]
Perchlorate	..[f]	88[e]	93[e]

[a] Phenacylpyridinium iodide and perchlorate have been repeatedly prepared and characterized in this Laboratory, King, THIS JOURNAL, **66**, 894 (1944). The substances reported in this table were compared with authentic specimens. [b] Based on the diazoketone. [c] For a description of the method see the experimental part. [d] Isolated as the iodide. [e] Isolated as the perchlorate. [f] Decomposed violently on heating.

The reaction was carried out in three ways, (a) by warming an intimate mixture of the amine salt and the diazoketone on the steam-bath, (b) by warming an alcoholic solution of the reaction components and (c) by warming an alcoholic solution of the reactants in the presence of an excess of the base.

A plausible explanation for these results may involve reversible addition of a proton to form the ion, (I).[2] I could then react with the base as



(1)

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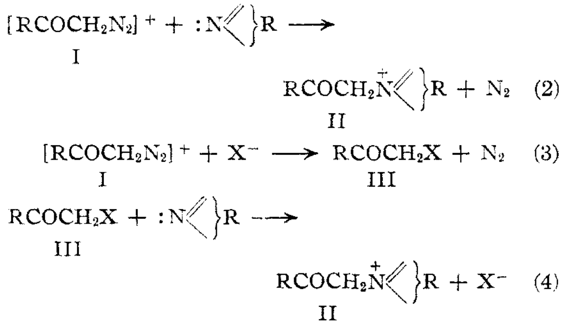
(1) For previous papers in this series dealing with quaternary salt formation, see King and co-workers, THIS JOURNAL, **70**, 242 (1948), and references therein.

(2) This is analogous to the explanation proposed by Hammett for certain reactions of diazoacetic ester with hydronium ions. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 288.



in 2 to produce II, or with X^- to form III, as in 3. III could subsequently react with the base to form the quaternary ion, (II), as shown in 4. In the case of the perchlorate salt, the reaction should certainly proceed by 2.

This investigation was supported by a grant from the Abbott fund of Northwestern University.

Experimental

Diazoacetophenone.—To an ether solution of diazomethane[3] was added, under cooling, a 1/3 molar portion of benzoyl chloride with efficient stirring. After the addition was complete the solution was stirred for an additional fifteen minutes and allowed to come to room temperature. The solvent and excess diazomethane were then distilled off carefully on the steam-bath, and the solution was cooled to effect crystallization. The material was recrystallized from petroleum ether until free of halogen, m. p. 49–50°.[4]

Heterocyclic Amine Salts.—2-Picoline hydriodide was prepared according to the directions of Murrill.[5] Quinoline hydriodide was prepared by the procedure of Trowbridge.[6] The sulfate, phosphate, perchlorate, tosylate and the hydrohalides of pyridine and the hydriodides of isoquinoline and 3-methyisoquinoline were prepared by adding a slight excess of the appropriate acid to the base and heating on the steam-bath overnight. The cooled suspension was filtered and the product washed with a small amount of absolute alcohol. The salts were used without further purification.

Preparation of the Quaternary Salts.—The three procedures used were essentially the same for all the compounds listed in this report. The techniques employed will be illustrated by a typical example for each of the methods.

(a) To 1.46 g. (0.010 mole) diazoacetophenone in 15 cc. of ether was added 2.07 g. (0.011 mole) of pyridine hydriodide. The ether was evaporated slowly on the steam-bath and the mixture heated for one-half hour after the vigorous evolution of nitrogen had occurred. The tarry material was then treated with a small amount of water and sufficient alcohol to bring it into solution at the boiling point, decolorized with charcoal, filtered and cooled. The 1-phenacylpyridinium iodide was recrystallized from dilute aqueous alcohol.

When salts of pyridine other than the hydriodide were used in the reaction (Table II), the hot aqueous alcoholic solution of the pyridinium salt was treated with perchloric acid and the product isolated as the sparingly soluble phenacylpyridinium perchlorate. The yields reported in Table II are calculated from the amount of perchlorate salt obtained in this manner.

(b) A mixture of 1.46 g. (0.010 mole) diazoacetophenone, 2.07 g. (0.011 mole) pyridine hydriodide and 15 cc. absolute alcohol was refluxed for one hour. A small volume of water was added, the solution was decolorized with charcoal and filtered. The quaternary iodide separated on cooling, and was recrystallized as above.

(c) To 1.46 g. (0.010 mole) diazoacetophenone in 15 cc. absolute alcohol was added 2.07 g. (0.011 mole) of pyridine hydriodide and 1.5 cc. of pyridine. The mixture was refluxed for one hour. A small amount of water was added and the product was crystallized as above.

Summary

It has been demonstrated that diazoacetophenone reacts with salts of certain heterocyclic amines to produce the corresponding phenacyl quaternary salt.

EVANSTON, ILLINOIS RECEIVED JULY 26, 1948

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[3] "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 50.

[4] Wolff, *Ann.*, **325**, 142 (1902).

[5] Murrill, THIS JOURNAL, **21**, 831 (1899).

[6] Trowbridge, *ibid.*, **21**, 67 (1899).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Oxygen Complexes on Charcoal[1a]

BY SOL WELLER[1b] AND T. F. YOUNG

Introduction

It is well known that treatment of activated charcoals with oxygen produces adsorbents having properties very different from those of the untreated charcoals. Rhead and Wheeler[2] were apparently the first investigators to adduce extensive evidence for the fixation of oxygen on the charcoal surface. They concluded that the formation of the loosely-formed physico-chemical complex is an important step in the combustion of carbon. A similar conclusion was reached by Lambert.[3] Lowry and Hulett[4] found that charcoal exposed to air at room temperature contained up to 3 to 4% oxygen; when the charcoal was outgassed at high temperatures, the oxygen was evolved as carbon monoxide and carbon dioxide.

From a study of the adsorption of acid and base adsorbed from dilute aqueous solution as a function of pressure of oxygen to which outgassed charcoal had been exposed, Schilow, Schatunowskaja and Tschmutow[5] suggested that there are at least three distinct surface oxides; Lepin[6] agreed with their suggestions. Two of these, they concluded, are formed by the adsorption of oxygen at room

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[1] (a) The work herein reported was done under a contract between the National Defense Research Committee and the University of Chicago. (b) Present address: U. S. Bureau of Mines, Bruceton, Pennsylvania.

[2] Rhead and Wheeler, *J. Chem. Soc.*, **103**, 461 (1913).

[3] Lambert, *Trans. Faraday Soc.*, **32**, 452 (1926).

[4] Lowry and Hulett, THIS JOURNAL, **42**, 1408 (1920).

[5] Schilow, Schatunowskaja and Tschmutow, *Z. physik. Chem.*, **A149**, 211 (1930); **A150**, 31 (1930).

[6] Lepin, *Physik. Z. Sowjetunion*, **4**, 282 (1933).