CHEMISTRY

Chairman: KEITH WHITE, Hanover College, QUENTIN PETERSEN, Wabash College, was elected chairman for 1964

ABSTRACTS

Some Reactions of Substituted Tetrahydrofuranones.¹ KEITH WHITE, RICHARD SCAMEHORN and ERLAND PORTER, Hanover College.—In the study of the asymmetric reduction of 2,5-dimethyl-2,5-diethyltetrahydro-3-furanone (I) and its oxime to the tetrahydro-3-furanol and the tetrahydrofuranyl amine, it was discovered that the cyclization of the furanone (I) was also stereospecific and that only one of the two possible racemates is obtained. It was postulated that only the least hindered form of I is stable enough to withstand the reaction conditions. As the first step in the determination of the configuration as either cis or trans diethyl, the ketone (I) was resolved by fractional crystallization from methanol and water of the brucine salt of the 4-carboxyphenyl-hydrozone. The conversion of the resolved ketone to methylethyl-diglycollic acid or to 2,5-dimethyl-2,5-diethyl-2,5-dihydrofuran without rearrangement is necessary to the proof of configuration. Routes to these compounds were reported.

Some Reactions of Benzoyl Isocyanate. JOHN W. McFARLAND, JAMES B. HOWARD¹ and J. THOMAS PARSONS,² DePauw University.— When Grignard reagents were added to ether solutions of benzoyl isocyanate a variety of products was obtained depending upon the nature of the organometallic used. Ethylmagnesium bromide and benzoyl isocyanate gave N,N'-dibenzoylurea, benzoylurea, and benzamide. Both isopropyl and tert. butyl Grignard reagents produced N, N'-dibenzoylurea and a product resulting from two moles of isocyanate and one mole of Grignard reagent. Naphthylmagnesium bromide and benzoyl isocyanate afforded naphthamide and a product which appeared to result from the combination of three moles of isocyanate with one mole of organomagnesium compound.

Benzoyl isocyanate reacted rapidly with triphenylcarbinol even at 0° C. The main products from the reaction were N,N'-dibenzoylurea and a compound representing two moles of isocyanate and one mole of triphenylcarbinol. The amounts of the two products were dependent upon temperature and the ratio of the two reagents. High temperature or high isocyanate concentration favored N,N'-dibenzoylurea formation. At 0°C. only the 2:1 isocyanate:carbinol product was obtained. This latter compound reacted with benzoyl isocyanate to give N,N'-dibenzoylurea among other products.

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The Use of Benzenesulfonyl Isocyanate as a Characterizing Reagent for Hindered Alcohols and Phenols. JOHN W. MCFARLAND and JAMES B. Howard,³ DePauw University.—Benzenesulfonyl isocvanate reacted rapidly with sterically hindered alcohols and phenols to give crystalline derivatives. Whereas phenyl isocyanate and tert, butyl alcohol reacted extremely slowly at 100°C. in toluene at 0.01 molar concentration each, benzenesulfonyl isocyanate and tert. butyl alcohol reacted instantaneously and completely at the same concentrations in toluene at 0°C. Derivatives have been facilely prepared from such sterically hindered alcohols as tert. butyl alcohol, tert. amyl alcohol, triethylcarbinol, and diphenyl-carbinol. The phenols which have been characterized by their reactions with benzenesulfonyl isocyanate include 2,6-di-tert. butylphenol, 2,6-di-isopropylphenol, 2,6-dimethoxyphenol, 2,6-dimethylphenol, 2,4,6-trinitrophenol (picric acid), 2-phenylphenol, 2-ethoxyphenol, and 4-tert. butylphenol. All of the above derivatives were the expected urethanes. Triphenylcarbinol also reacted readily with benzenesulfonyl isocyanate at temperatures from 56°C. to 100°C. The chief product from this reaction, however, was N-(triphenylmethyl) benzenesulfonamide which apparently resulted from the decarboxylation of the normal addition product.

Hammett Acidity Functions of Some Organophosphorus Acids. A. GILBERT COOK, Valparaiso University.—The Hammett acidity functions of several organophosphorous acids at various concentrations have been determined in ethylene glycol solvent. They are compared with pK_a determinations as measures of relative acidities. The use of dimethyl sulfoxide as a medium for Hammett acidity function determinations is also discussed.

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