

A Ketenimine from the Addition of a Carbene to an Isocyanide

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Although carbenes and isocyanides, two formally divalent species, might be expected to react with each other to give ketenimines, only one attempt to demonstrate such an addition appears to have been recorded. Dichlorocarbene, generated from potassium trichloroacetate in alcohols, reacts with cyclohexyl isocyanide to give *N*-cyclohexyldichloroacetimidates, the adducts of alcohols to dichloroketene-*N*-cyclohexylimine.¹ We find that the ketenimine **1** is obtained in 51% yield on thermolysis of methyl phenyldiazoacetate in *t*-butyl isocyanide (Scheme I). An authentic

Phenylmethoxycarbonylketene-*N*-*t*-butylimine.—A mixture of 6.55 g of methyl triphenylphosphoranylidenebenzylacetate⁴ and 20 ml of *t*-butyl isocyanate, contained in a sealed Carius tube, was stirred at 103° for 24 hr. The excess *t*-butyl isocyanate was removed under vacuum; ethyl acetate (15 ml) was added to the residue; the mixture was heated to the boiling point, cooled, and filtered. The solids were washed with ethyl acetate and dried to give 3.38 g of triphenylphosphine oxide, identified by its infrared spectrum. The combined filtrates were concentrated to dryness, and the residue was short-path distilled at a bath temperature of 100–130° (0.2 μ) to give 3.39 g (92% yield) of phenylmethoxycarbonylketene-*N*-*t*-butylimine as a very pale yellow oil: uv max (cyclohexane) 300 mμ (sh, ε 5500), 268 (10,000), and 243 (9300); ir (CCl₄) 2040 and 1710 cm⁻¹, among others; nmr (CDCl₃) τ 2.0–2.7 (m, 5, phenyl), 6.0 (s, 3, COOMe), and 8.2 (s, 9, CMe₃). Anal. Calcd for C₁₄H₁₇NO₂: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.41; H, 7.66; N, 5.83.

Registry No.—1, 22979-24-4.

(4) H. J. Bestmann and H. Schulz, *Ann.*, **674**, 11 (1964).

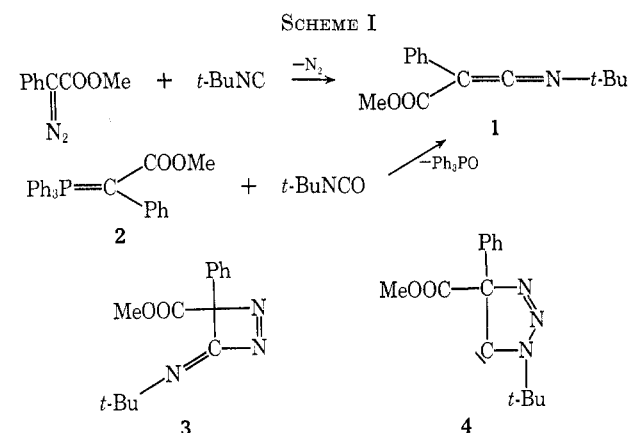
α-Aryl- and α-Cyanodiazooacetic Esters

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For a study of the effect of substituents on the norcaradiene-cycloheptatriene equilibrium,¹ we required, among others, methyl phenyldiazoacetate (**2a**) and its *p*-methoxy (**2b**) and *p*-nitro derivatives (**2c**), as well as methyl cyanodiazooacetate (**5**). Impure ethyl phenyldiazoacetate has been prepared in poor yield by diazotization of ethyl phenylglycinate.² The Bamford-Stevens reaction of methyl phenylglyoxylate *p*-toluenesulfonylhydrazone has been reported³ to give methyl phenyldiazoacetate (**2a**), also of only 63% purity. Ethyl *p*-nitrophenyldiazoacetate has been prepared by reaction of *p*-toluenesulfonyl azide with ethyl *p*-nitrophenylacetate.⁴ We find that pure methyl phenyldiazoacetate (**2a**) can be obtained in 89% overall yield from commercially available methyl phenylglyoxylate *via* lead tetraacetate oxidation⁵ of the hydrazones **1a** (Scheme I). Reaction of methyl phenylglyoxylate with hydrazine in glacial acetic acid gave a mixture of two isomeric hydrazones **1a** in a ratio of 60:40.⁶ The two isomers could be separated; the major isomer was assigned the intramolecularly hydrogen-bonded *syn*⁷ structure on the basis of its lower boiling point, the lower field chemical shift of the amino protons (τ 1.5 *vs.* 3.8 in the *anti* isomer), and the insensitivity of the N–H



sample of **1** was prepared by a Wittig reaction between *t*-butyl isocyanate and the phosphorane **2**. On the basis of the available evidence, it cannot be ruled out completely that the diazo ester initially adds to *t*-butyl isocyanide to form intermediates such as **3** or **4**, which then lose nitrogen to give **1**. However, the most likely reaction path involves initial nitrogen loss from methyl phenyldiazoacetate followed by α addition of phenylmethoxycarbonylcarbene to *t*-butyl isocyanide, especially since the reaction requires heating to a temperature at which methyl phenyldiazoacetate is known² to decompose with loss of nitrogen.

Experimental Section

Thermolysis of Methyl Phenyldiazoacetate in *t*-Butyl Isocyanide.—A mixture of 3.10 g of methyl phenyldiazoacetate⁸ and 8.87 g of *t*-butyl isocyanide was placed in a Carius tube. The tube was sealed under vacuum and heated to 140° for 6 hr. Removal of the excess isocyanide and short-path distillation of the residue at 120–140° bath temperature (2 μ) gave 2.07 g (51%) of phenylmethoxycarbonylketene-*N*-*t*-butylimine, identified by comparison of its infrared and nmr spectra with those of an authentic sample (see below).

(1) A. Halleux, *Angew. Chem.*, **76**, 889 (1964).
 (2) E. Ciganek, unpublished observation.
 (3) E. Ciganek, *J. Org. Chem.*, **35**, 862 (1970).

(1) The synthesis and structure determination of the benzene adducts of the carbenes derived from the diazo compounds described in this note will be the subject of a forthcoming publication.

(2) T. Curtius and E. Müller, *Ber.*, **37**, 1261 (1904); cf. A. Kossel, *ibid.*, **24**, 4145 (1891).

(3) I. Moritani, T. Hosokawa, and N. Obata, *J. Org. Chem.*, **34**, 670 (1969).

(4) W. Pelz, U. S. Patent 2,950,273 (1960); *Chem. Abstr.*, **55**, 2116 (1961); (b) M. Regitz, *Chem. Ber.*, **98**, 1210 (1965).

(5) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

(6) One of the two isomers of **1a** has recently been prepared by a more circuitous route: H. Neunhoeffer, *Ann. Chem.*, **722**, 38 (1969); no stereochemistry was assigned but on the basis of the reported melting point it appears to be the *anti* isomer.

(7) The terms *syn* and *anti* refer to the relationship of the amino to the methoxycarbonyl group in **1**.