Amidomethylation of Trichloroethylene and Acetylene: Syntheses of N-Protected α -Chloro- β -alanines and β -Aminopropanals

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Summary The reaction of amidomethyl cations with trichloroethylene or acetylene in sulphuric acid affords the corresponding β -amido- α -chloropropionic acids and β -amidopropanals.

THE successful addition of carbonium ions to the weakly



basic trichloroethylene in sulphuric acid as solvent has been reported to require temperatures above 80°.1,2 The reactants, in order to be sufficiently stable under such conditions, were restricted to the 1-adamantyl, 2-norbornyl, substituted benzyl, and diphenylmethyl cations. We now report a convenient synthesis of the hitherto unknown β -amido- α -chloropropionic acids (IIIa), (IIIb), and (IIIc) from the appropriate amidomethanols (Ia-c) and trichloroethylene (yields 73-91%).

In these reactions, which proceed at unexpectedly low temperatures (40-50°), the short-lived intermediate (II) undergoes a spontaneous solvolysis to (III). Instead of the carbinols (I), other amidomethylating agents, such as the methylene-bis-amides or mixtures of formaldehyde and amides,³ may be used. A solution of (Ia) (0.565 moles) in 95% sulphuric acid (320 ml.) was stirred with trichloroethylene (1.14 moles) for 4 hr. at 48°. After being poured on to ice, the product (IIIa) (91%) was obtained by filtration.

Another process, the amidomethylation of acetylene at atmospheric pressure, offers a simple route to β -amidopropanals. On being stirred in 96% sulphuric acid for a few min., the methanols (Ia-c) react with equimolar amounts of acetylene below room temp. (5-10°). It is assumed that the key step consists of the formation of the highly reactive 2-amidomethylvinyl cations (IV).

Although the stabilization pathway of (IVc) has not yet been studied, the corresponding species (IVa) and (IVb) are known to be converted (80-82%) into the amidomethylacetaldehydes (Va) and (Vb). As has been shown by the analogous syntheses of 1-adamantylacetaldehydes⁴ and exo-norbornylacetaldehyde,⁵ the generation of (V) does not necessitate any participation of the carbonyl group in the intermediate (IV). β -Phthalimidopropanal (Va), m.p. 125-126° (recrystallized from water), was identified by comparison with an authentic sample⁶ and by oxidation to β -phthalimidopropionic acid." Because of its rapid polymerization, (Vb) could not be isolated in the pure state.

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- ³ H. E. Zaugg and W. B. Martin, Org. Reactions, 1965, **14**, **63**. ⁴ K. Bott, *Tetrahedron Letters*, 1969, 1747.
- ⁵ K. Bott, unpublished results.
- ⁶ R. O. Atkinson and F. Poppelsdorf, J. Chem. Soc., 1952, 2448.

7 This compound is readily obtainable by phthalimidomethylation of 1,1-dichloroethylene in sulphuric acid: Dr. W. Kriesten, Chemische Werke Hüls, unpublished results.