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

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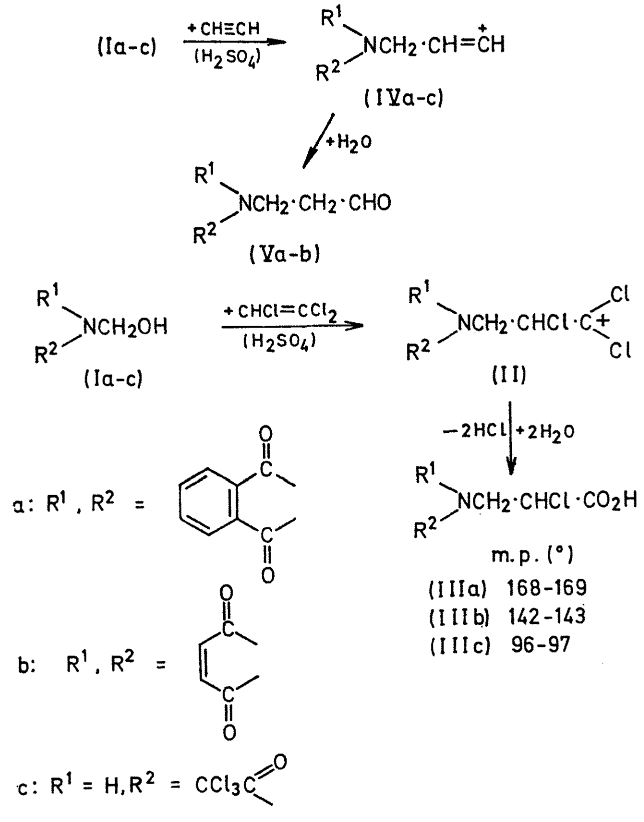
Summary The reaction of amidomethyl cations with trichloroethylene or acetylene in sulphuric acid affords the corresponding β-amido-α-chloropropionic acids and β-amidopropanals.

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%).



	m.p. (°)
(IIIa)	168-169
(IIIb)	142-143
(IIIc)	96-97

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-adamantylacetaldehydes[4] 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 sample[6] and by oxidation to β-phthalimidopropionic acid.[7] Because of its rapid polymerization, (Vb) could not be isolated in the pure state.

(*Received, August 27th,* 1969; *Com.* 1320.)

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[1] K. Bott, *Angew. Chem.*, 1967, **79**, 943; *Angew. Chem. Internat. Edn.*, 1967, **6**, 946.

[2] K. Bott, *Tetrahedron Letters*, 1968, 4979.

[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.