

REACTIONS OF ORGANIC ANIONS. XLIII.* CATALYTIC METHOD
FOR SYNTHESIS OF GLYCIDIC NITRILES IN AQUEOUS MEDIUM

A.Jończyk, M.Fedoryński and M.Mąkosza

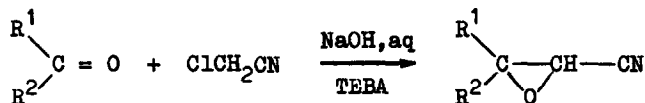
Institute of Organic Chemistry and Technology,
Technical University (Politechnika), Warsaw, Poland

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Darzens condensation between α -halocarbanions and carbonyl compounds that leads to the formation of glycidic acid derivatives is useful tool in synthesis. Generally the α -halocarbanions are generated by action of dry sodium alkoxides, amide, hydride or other such agents on α -haloesters, nitriles, ketones etc. in strictly anhydrous organic solvent or liquid ammonia (1).

As we showed earlier many reactions involving carbanions that were believed to require strictly anhydrous conditions and strong basic agents, can be performed in the presence of aqueous NaOH and quaternary ammonium catalyst (the most convenient seems to be triethylbenzylammonium chloride - TEBA). These conditions are very useful for alkylation of C-H acids (2) (arylacetonitriles, cyclopentadiene hydrocarbons, some ketones etc.), generation of trihalomethylanions and halocarbenes (3) etc.

Now we would like to report that this basic system is also sufficient for generation of halocyanomethylanion and its condensation with carbonyl compounds giving rise to the formation of glycidic nitriles (4).



* Part XLII. See preceding paper.

For example when chloroacetonitrile (7.6 g, 0.1 mole) was added dropwise to the vigorously stirred mixture of cyclohexanone (10.8 g, 0.11 mole), 50 % NaOHaq (20 ml) and TEBA (0.4 g) and reaction was carried out for 30 min. at 15-20° ordinary working up gave 1-oxaspiro[2,5] octane-2-carbonitrile (10.8 g, yield 79 %) b.p. 87°/5 mm Hg.

Similarly the following glycidic nitriles were obtained (R¹, R², yield, b.p.): C₆H₅, H, 75 %, 119-121°/6; CH₃, CH₃, 60 %, 47°/12; C₆H₅, CH₃, 80 %, 115-121°/6; -(CH₂)₄, 65 %, 76°/6; -(CH₂)₄CH-, 78 %, 93-95°/5; C₆H₅, C₆H₅, 55 %, m.p. 72-73°.

Asymmetric ketones, like acetophenone, or aldehydes can form two stereoisomers. In the most cases both isomers were obtained as showed by NMR. From the mixture of 3-phenylglycidonitriles crystalline cis isomer was isolated m.p. 55-57°

In the case of more acidic ketones, like desoxybenzoine or phenylacetone anion of ketone and not that of chloroacetonitrile is rather formed that leads to the alkylation similar to the described in our previous papers (2,5) e.g. from phenylacetone 3-phenyllevulinonitrile (yield 45 %), m.p. 94-95° was formed.

Some dipolar aprotic solvents (HMPT, DMF, DMSO), that are known to accelerate many reactions with carbanions can be used instead of ammonium catalyst. Results of the reactions between chloroacetonitrile and carbonyl compounds in the presence of aqueous NaOH and these solvents are very close to the obtained in catalytic reaction.

All compounds described in this paper have physical data in agreement with those reported. Their NMR spectra showed pattern characteristic for the structure.

R e f e r e n c e s

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