

Cyanohydrins

Q 0521

52- 088

Enantioselective and Diastereoselective Syntheses of Cyanohydrin Carbonates.

— Alkyl cyanoformates add to a range of aldehydes in the presence of catalyst (I) to give highly enantio- and diastereomerically enriched cyanohydrin carbonates. The use of either solid KCN or 18-crown-6·KCN as co-catalyst allows a decrease to 1.5 - 2 mol% of (I). A new and general synthesis of chiral alkyl cyanoformates involves the treatment of appropriate alcohols with oxalyl chloride and subsequent dehydration of the intermediate oxamides (to be continued). — (BELOKON, Y. N.; CLEGG, W.; HARRINGTON, R. W.; ISHIBASHI, E.; NOMURA, H.; NORTH*, M.; Tetrahedron 63 (2007) 39, 9724-9740; Sch. Nat. Sci., Univ. Newcastle, Newcastle upon Tyne NE1 7RU, UK; Eng.) — Klein

$$R^{1}-CHO \xrightarrow{Et-O^{-}CN \ (III), \ A)} = 0$$

$$R^{1}-CHO \xrightarrow{Et-O^{-}CN \ (II), \ A} = 0$$

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$$R^{2}-CHO \xrightarrow{\text{(III), A)}} 1.5 \text{ mol% } I^{*}/1 \text{ mol% } 18-crown-6\cdot KCN (cat.)} \\ V \\ Me \\ CN \\ S)-VI \\ AR^{2}: \longrightarrow 100\% (97\% \text{ e.e.}) \\ CR^{2}: \longrightarrow 100\% (100\% \text{ e.e.}) \\ CR^{2}: \longrightarrow 100\% (97\% \text{ e.e.}) \\ CR^{2}: \longrightarrow 100\% (97\% \text{ e.e.}) \\ CR^{2}: \longrightarrow 100\% (93\% \text{ e.e.}) \\ CR^{2}: \longrightarrow 100\% (9$$



$$\begin{array}{c} \text{OH} \\ \text{Me} \\ \text{E} \\ \end{array} \begin{array}{c} 1. \text{ CI} \\ \text{OVII} \\ \text{E: -CO-0-Et} \\ \text{B): CH}_2\text{CI}_2, \ 0 -> +25^{\circ}\text{C} \ \text{C): conc. aq. NH}_3, \ \text{CH}_2\text{CI}_2, \ 0^{\circ}\text{C} \\ \end{array} \begin{array}{c} \text{D)} \\ \text{Me} \\ \text{E} \\ \end{array} \begin{array}{c} \text{CN} \\ \text{Me} \\ \text{E} \\ \end{array} \begin{array}{c} \text{CN} \\ \text{78\%} \\ \text{B): CH}_2\text{CI}_2, \ 0 -> +25^{\circ}\text{C} \ \text{C): conc. aq. NH}_3, \ \text{CH}_2\text{CI}_2, \ 0^{\circ}\text{C} \\ \end{array} \begin{array}{c} \text{D): Py, TFAA, CH}_2\text{CI}_2, \ 0 -> +25^{\circ}\text{C} \\ \text{CN} \\ \text{XI*} \\ \end{array} \begin{array}{c} \text{CN} \\ \text{XII*} \\ \text{G 32\% (12.3:1)} \\ \text{g 28\% (10.8:1)} \end{array}$$