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A NOVEL METHOD FOR THE DEGRADATION OF α-UNBRANCHED CARBOXYLIC ACIDS INTO ALDEHYDES CONTAINING ONE CARBON ATOM LESS

Gábor Doleschall

Research Group of Alkaloid Chemistry of the Hungarian Academy
of Sciences, 1111 Budapest, HUNGARY

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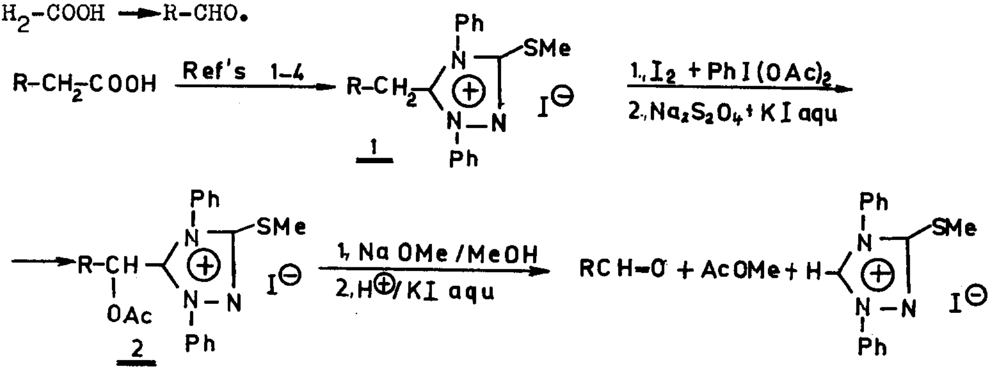
In continuation of our studies[1-4] of the utilization of s-triazol derivatives for synthetic purposes, a simple and selective method, outlined in the Scheme depicted below, has been devised for effecting the transformation $R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CHO$.



The resulting aldehydes were identified in the form of their condensation products with 6-(2-aminophenyl)-3-methylthio-as-triazin-5(2H)-one[5] or as the 2,4-dinitrophenylhydrazones on the basis of the IR, NMR and mass spectra and microanalyses,[6] and, if available, by comparison with authentic samples. The overall yields are shown below.

$R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CHO$

R	1	overall yield
Me	Ref's 1,2,4	31% [7]
Et	Ref's 1,2,4	56% [7]
$n\text{-}C_7H_{15}$	m.p. 141-2° (83%)	41% [8]
$MeOOC\text{-}(CH_2)_3\text{-}$	m.p. 147° (72%)	37% [8]
$Ph\text{-}CO\text{-}(CH_2)_2\text{-}$	m.p. 229-30° (88%)	34% [7]
$(\underline{Z})\text{-}C_8H_{17}\text{-}CH{=}CH\text{-}(CH_2)_6$	m.p. 114° (80%)	19% [8]

Selective α-acetoxylations were effected by adding the $CHCl_3$ (250 ml) soln of 0.12 mole $PhI(OAc)_2$ [9] under stirring to the refluxing solns of 0.1 mole of the compounds **1** and 0.11 mole of I_2 in 100 ml $CHCl_3$ (15 min) and further refluxing for 30 min. The mixtures were washed with the aqu (300 ml) soln of $Na_2S_2O_4$ (45 g), KI (90 g) and AcOH (30 ml), and with water. Evaporation *in vacuo*, drying by azeotropic distillation with CH_2Cl_2 and trituration with ether furnished the compounds **2** which were reacted at r.t. for 15 min with 0.08 mole NaOMe in MeOH (100 ml). The aldehydes were isolated after acidification (H_2SO_4 or AcOH) by steam distillation or by extraction (ether,pentane).

The key-step of the sequence is the selective α-acetoxylation of the compounds **1**, and is highly dependent on the anion present. *E.g.* the chloride and fluorborate corresponding to **1** did not react under the above conditions, the oxydation of the iodides themselves is less general and only the oxydation of the triiodides proved satisfactory. The required α-acyloxylated products could not be obtained by reacting the compounds **1** with $Tl(OAc)_3$, $Pb(OAc)_4$, $R\text{-}CO_3H$ etc.

The structures of the intermediates **2** were proven by comparison of **2**, R = Me (m.p. 185-186°; 61% yield) with an authentic sample. [3] For the cleavage of the compounds **2**, *cf*. Ref. 3.

If $R\text{-}CH_2\text{-}COOH$ contains an active hydrogen atom in the β-position, the α,β-didehydrogenated rather than the α-acetoxylated product is obtained on treatment with $PhI(OAc)_2$. *E.g.* **1** (R = $MeOOC\text{-}CH_2$)[3] furnishes the (*E*)-2-carbomethoxyvinyl derivative (m.p. 219-20°, 59% yield). No acetoxylation takes place if the alkyl group of **1** is branched in α-position (isopropyl analog[2] of **1**), and only tars were formed from **1** (R = Ph [1]).

References and Notes

1. G. Doleschall, Tetrahedron Letters, No. 31, 2649 (1974)
2. G. Doleschall, Tetrahedron Letters, No. 9, 681 (1975)
3. G. Doleschall, Tetrahedron Letters, No. 24, 1889 (1975)
4. G. Doleschall, Tetrahedron, in press
5. G. Doleschall and K. Lempert, Tetrahedron **29**, 639 (1973); **30**, 3997 (1974)
6. All new compounds gave satisfactory microanalytical results.
7. Condensation product with 6-(2-aminophenyl)-3-methylthio-*as*-triazin-5(2*H*)-one
8. Pure distilled aldehyde
9. K.H. Pausacker, J. Chem. Soc. 1953, 107