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6-METHYLENE CYCLOHEXANONE-2,4-DICARBOXYLATES FROM THE ANIONS OF SECONDARY AMIDES AND ACRYLATES

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6-Methylene cyclohexanone-2,4-dicarboxylates as their enol tautomers[1] (3) are the major products from condensation of the anions of secondary amides with acrylates.

In an attempt to make 2 (R^1=Et, R = allyl), ethyl acrylate was added to the anion of N-allyl benzamide (1, R = allyl) generated with NaH (1 mol.) in DMF at 0°C. The major product (60% based on acrylate), isolated as a pure liquid after chromatography on silica gel, was assigned the structure 3 (R^1 = Et), ν_{max} (film) 1735, 1665, 1640, 1600cm^{-1}; violet colour with $FeCl_3$; M^+ 254 ($C_{13}H_{18}O_5$); δ_H ($CDCl_3$) 1.26 (3H,t,ester CH_3), 1.32 (3H,t,ester CH_3), 2.2 → 2.8 (5H, br, 2 CH_2's and $>\underline{CH}-CO_2Et$), 4.22 (2H, q, ester CH_2), 4.3 (2H, q, ester CH_2), 5.32 and 5.96 (2H, $>=CH_2$), 12.0 (1H, OH). Other secondary amide anions can act as initiators of these acrylate condensation reactions. With N-methyl benzamide (1, R = Me) and ethyl acrylate, 3(R^1 = Et) was again the major product (~ 60% yield). When 1 (R = Me) and methyl acrylate were the reactants, crystalline products were isolated but the reaction was more complex. The structure of 3 (R^1 = Me), m.p. 68 - 70°C, obtained in 55% yield, was supported by partially decoupled ^{13}C n.m.r. - δ_c 25.9 (t, $-CH_2-$), 33.2 (t, $-CH_2-$), 39.2 (d, $-\underline{CH}-CO_2Me$), 52.5 (2q, ester Me's), 98.1 (s, = $\underline{C}-CO_2Me$), 117.2 (t, $=CH_2$), 136.5 (s, $-\underline{C}=CH_2$), 163.5, 172.6 and 174.1 (3s, 3 $>C = O$).

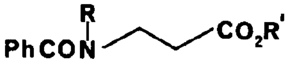
An aromatic amide, $C_{19}H_{23}NO_6$, m.p. 106 - 107°C, was also isolated in 12% yield and spectral data supported structure 4 - δ_c 26.1 (t, $-CH_2-$) 27.6 (t, $-CH_2-$), 28.8 (t, $-CH_2-$), 39.9 (q, $-\overset{|}{N}-CH_3$), 46.6 (s, $>\overset{|}{\underline{C}}-CO_2Me$), 51.4 (q, $-O-CH_3$), 52.2 (q, $-O-CH_3$) 55.2 (t, $-CH_2-\overset{|}{N}-$), 95.3 (q, $=\overset{|}{\underline{C}}-CO_2Me$), 126.8 (2d, o- or m- aromatics), 128.3 (2d, o- or m- aromatics) 129.5 (d, p aromatic c), 136.3 (s, Ph $\underline{C}O-$), 170.7, 172.2, 172.4 and 174.9 (4s, 4 C = O's); δ_H 2.1-2.6 (5H, complex; 2H at C5, 2H at C6, 1H of AB quartet at C3), 2.95 (3H, s, $-\overset{|}{N}-CH_3$), 2.97 (1H of AB quartet at C3), 3.72 (3H, s, ester CH_3), 3.77 (3H, s, ester CH_3), 3.8 (2H, $-\overset{|}{\underset{|}{C}}-CH_2-N-$ AB quartet), 7.41 (5H, aromatic). The n.m.r. spectra of 4 indicate some restricted rotation in the geminal substituents at C4. The room temperature ^{13}C n.m.r. showed the $-\overset{|}{N}-\underline{CH}_3$ and $-\overset{|}{\underset{|}{C}}-\underline{CH}_2-\overset{|}{N}-$groups as weak broad signals which sharpened considerably at 54°C.

The structure 5 was assigned to a further product, $C_{12}H_{18}O_6$, m.p. 73 - 74°C obtained in 5% yield. Compared with 3(R' = Me), 5 lacked the exocyclic methylene group but had an additional -OMe singlet at δ 3.29 and a two proton singlet ($-\underline{CH}_2-OMe$) at δ3.42. The ^{13}C n.m.r. bore strong similarities to that of 4 - δ C 26.0 (2t, 2-CH_2-), 27.7 (t, $-CH_2-$), 46.3 (s, $>\overset{|}{\underline{C}}-CO_2Me$), 51.3 (q, $CO_2\underline{Me}$), 52.0 (q, $CO_2\underline{Me}$), 59.3 (q, $-CH_2-O-\underline{CH}_3$), 77.4 (t, $-\underline{CH}_2-O.CH_3$), 95.2 (s, = $\overset{\cdot}{\underline{C}}.CO_2Me$), 170.5, 172.2, 174.7 (3s, 3C = O).

Presumably 3 arose from 1 via route (a) of scheme A (where X = $Ph.CO.\overset{Me}{N}$ - or $Ph.\overset{O^-}{C}=N.Me$) and route (b) is a possible source of 4. The shunt c gives an opportunity for the methoxide ion generated in the Dieckmann condensation to add to the conjugated ester and thus provide the intermediates for 5. 4 could not be converted directly to 5 with sodium methoxide in D.M.F. under conditions close to those of the reaction.

PhCONHR

1



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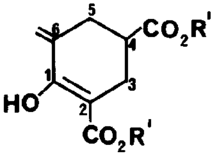

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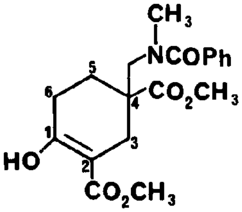

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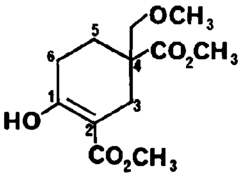

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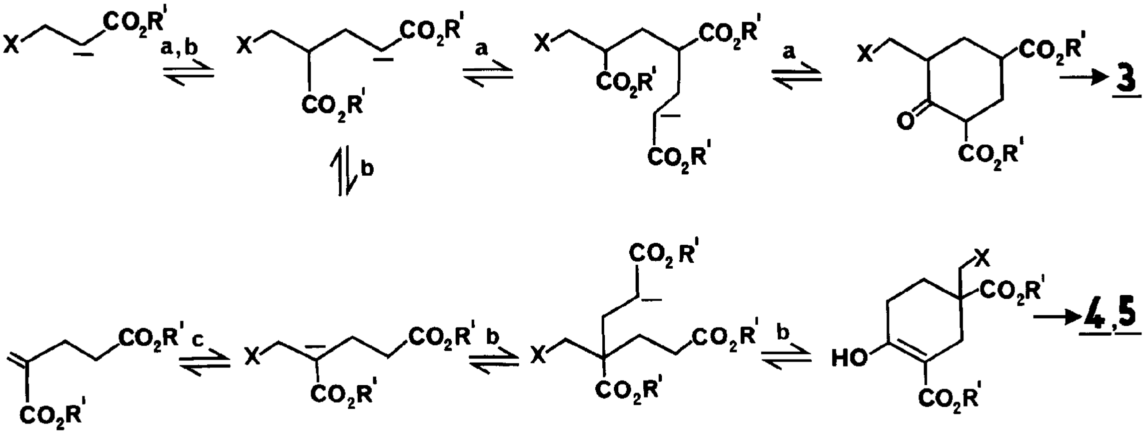
Scheme A



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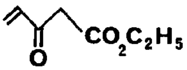
References

1. Nazarov reagents, e.g. ethyl acryloylacetate are 50% enolised, c.f., L.Pichat and J.P. Beaucourt, Synthesis, 537, 1973.



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