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# THE REACTION OF AMINES WITH METHYL PROPIOLATE

W. Bottomley

Division of Plant Industry, C.S.I.R.O. Canberra, Australia.

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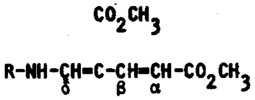
The addition of amines to acetylenes has been the subject of a number of studies(1,2,3) However, the only products described have been 1:1 adducts. In the course of a study of the addition of 2-aminopyridines to methyl propiolate(4), it was found that the compounds which had been previously described as having one molecule of the methyl propiolate added to each nitrogen atom of the amino pyridine had, in fact, both residues attached to the primary amino group (I, R=2-pyridyl). In order to determine whether or not this reaction was a general one, the reaction between a number of other amines and methyl propiolate was investigated.

It has now been found that addition of methyl propiolate to either primary or secondary amines in the cold generally resulted in 1:1 adducts of the type previously described(1,2,3) However heating primary amines at 100° with excess methyl propiolate resulted in the formation of products which were shown by N.M.R. (Table 1) and infra-red spectroscopy, to be diadducts of the structure I. The N.M.R. spectra exhibited an AB quarted at 6 & 8 p.p.m. with a coupling constant of 16 c.p.s. typical of trans vinyl protons. In addition a second AB quartet was centred around 8 & 10 p.p.m. (J = 13-14 c.p.s.) with the lower field doublet being very broad. This broad doublet slowly disappeared on deuteration indicating that it was probably caused by an amine proton, a fact which was supported by the presence of a broad absorption band near 3260 $cm^{-1}$ in the infra-red spectrum. The diadduct from aniline exhibited a clear 0.6 c.p.s. long-range coupling between the $\beta$ & $\delta$ protons of the conjugated carbon chain. This was not detected in the spectra of diadducts from aliphatic amines, but otherwise these spectra were similar to that of the aniline derivatives. Structure (I) is the only structure consistent with the above data.

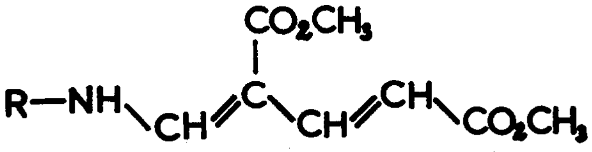
TABLE I

Melting points and N.M.R. data of diadducts

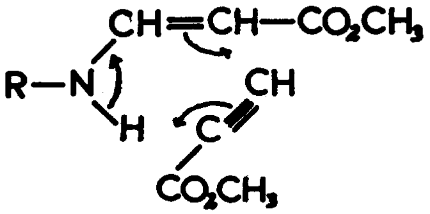


$$R\text{-}NH\text{-}\underset{\delta}{C}H{=}\overset{CO_2CH_3}{C}\text{-}\underset{\beta}{C}H{=}\underset{\alpha}{C}H\text{-}CO_2CH_3$$

| R | m.p. (5) | Chemical shift (p.p.m.) | | | | $J_{\alpha\beta}$ | $J_{N\delta}$ |
|---|---|---|---|---|---|---|---|
| | | α | β | δ | N | | |
| Me- | 143.4° | 6.02 | 7.43 | 7.23 | 8.75 | 16 | 14 |
| Ph- | 118.9° | 6.23 | 7.50 | 7.73 | 10.75 | 16 | 13 |
| Ph-$CH_2$- | 108.9° | 6.03 | 7.40 | 7.30 | 9.20 | 16 | 13 |
| cyclo $C_6H_{11}$- | 99-100° | 6.00 | 7.45 | 7.35 | 9.00 | 16 | 14 |



I



II

In the compounds from methylamine and benzylamine, the coupling constant between the -NH- and the adjacent methyl or methylene protons was 6 c.p.s.

In addition to the broad N-H absorption the infra-red spectra of the diadducts revealed two carbonyl bands - one about 1700 $cm^{-1}$ assigned to the terminal carbomethoxy and one 1670-1665 $cm^{-1}$, due to the hydrogen bonded carbomethoxy of the β-aminoacrylic ester moiety. This low frequency ester carbonyl was also a feature of the spectra of cis β-aminoacrylic esters (3) due to the hydrogen bonding between the carbonyl and the amino groups and hence these two groups must also be cis to one another in the diadducts.

Since no diadducts were obtained from secondary amines and the monoadducts could be converted to diadducts by heating with methyl propiolate, it seems probable that the first step in the formation of the diadducts is the synthesis of the monoadducts and that the addition of the second molecule of methyl propiolate involves the -NH- group in a mechanism such as is shown in II followed by a proton migration to yield I.

In general the amine was cooled in ice and 2 moles of methyl propiolate added slowly. The mixture was then heated in a closed vessel at 100° for 4 hours and the product recrystallized from methanol. If necessary the diadduct could usually be separated from any monoadduct by extracting a chloroform solution with N.HCl when the very weakly basic diadduct remained in the chloroform. The diadduct from methylamine was prepared by heating methyl β-methylaminoacrylic ester with one mole of methyl propiolate. The β-methylaminoacrylic ester was obtained by adding one mole of methyl propiolate to a cooled solution of methylamine in ethanol.

REFERENCES

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(4) J.G. Wilson and W. Bottomley, in press.

(5) Satisfactory analyses were obtained for all compounds.