Tetrahedron Letters No.52, pp. 6413-6417, 1966. Pergamon Press Ltd.
Printed in Great Britain.

A FACILE AMINO-CLAISEN REARRANGEMENT

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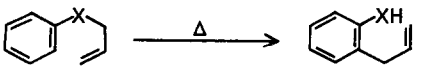
(Received 1 October 1966; in revised form 21 October 1966)

Extension of the Claisen rearrangement of phenyl allyl ethers (1, 2) to structural analogues, in which the ether oxygen (X=O) has been replaced by other groups or atoms, has met very limited success. The case of thio-Claisen rearrangement*, in which X is sulfur, was unsuccessful (3, 4) until recently when it was discovered that allyl phenyl sulfide rearranges to 2-methylthiacoumaran and thiachroman in boiling quinoline (5, 6, 7). In the preceding communication (8), we reported an additional example of this type, in which allyl 4-quinolyl sulfides transformed into 2-methyl-2,3-dihydrothieno-[3,2-c]quinolines probably via intermediates, 3-allyl-4(1H)-quinolinthiones.



The case of amino-Claisen rearrangement,* in which X is NH group, also has failed (9, 10, 11), viz., pyrolysis of N-allylaniline at 275° gives aniline and propylene as major products (9). However, Marcinkiewicz et al. (12) have reported only one successful case of the amino-Claisen rearrangement, in which N-allyl-1-naphthylamine rearranges at 260° to 2-allyl-1-naphthylamine, and they have suggested that some selective reaction systems would undergo the amino-Claisen rearrangement without

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* These names have been designated by Prof. Kwart (see ref. 7).

decomposition, since the amino-Claisen rearrangement must require an additional activation energy of about 6 Kcal/mole than that in oxy-Claisen rearrangement.* We wish to report a facile amino-Claisen rearrangement of 1-phenyl-2-allyl-3-pyrazolin-5-ones.

Alkylation of 1-phenyl-3,4-dimethyl-2-pyrazolin-5-one with allyl bromide resulted in the formation of 2-allyl-1-phenyl-3,4-dimethyl-3-pyrazolin-5-one (Ia), as an oil (13) and 4-allyl-1-phenyl-3,4-dimethyl-2-pyrazolin-5-one (IIa), b.$p_{0.8}$ 130-131°, in a ratio of ca. 1 to 2. Similarly, 1-phenyl-3-methyl-2,4-diallyl-3-pyrazolin-5-one (Ib) as an oil (13) and 1-phenyl-3-methyl-4,4-diallyl-2-pyrazolin-5-one (IIb), b.$p_{0.05}$ 129-130°, were prepared by the allylation of 4-allyl-1-phenyl-3-methyl-2-pyrazolin-5-one. Structures of these products were determined by IR and UV spectral analyses as shown in Table I. For example, the N-2 allyl compound Ia had $\nu_{C=O}$ 1658 cm^{-1} and λ_{max} 247 mμ (log ε 4.10) and 275 (3.96), characteristic of the fixed [1H, 2H]pyrazolin-5-one derivatives (14). On the other hand, the C-4 allyl compound IIa had $\nu_{C=O}$ 1707 cm^{-1} and λ_{max} 242 mμ (log ε 4.21) characteristic of the fixed [1H, 4H]-pyrazolin-5-one derivatives (14). Moreover, IIa and IIb were identical with the samples obtained by condensation of ethyl 2-acetyl-2-methyl-4-pentenoate and ethyl 2-acetyl-2-allyl-4-pentenoate with phenylhydrazine, respectively.

Both the N-2 allyl compounds, Ia and Ib, were thermally unstable and vacuum distillation of these compounds afforded a mixture of I and II. Complete rearrangement of I to II was accomplished by heating at 180° for 30 min. Thus, Ia and Ib rearranged to IIa and IIb, respectively, in quantiative yields. This allyl migration reaction is corresponding to the amino-Claisen rearrangement.

In order to confirm whether or not this allyl migration proceeds through a six-membered cyclic transition state with inversion of a migrating allyl group, thermal rearrangement of N-2-crotyl compound was examined. Alkylation of 1-phenyl-3,4-

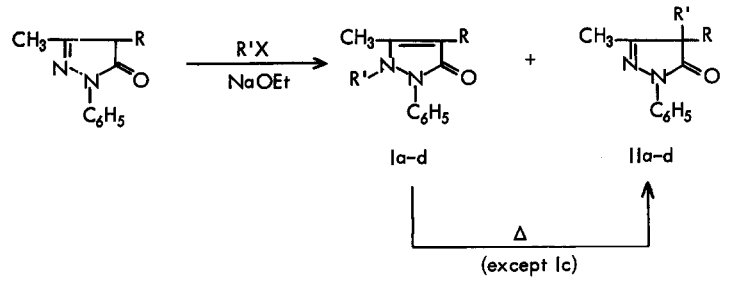
TABLE I
IR and UV Spectral Data of Pyrazolin-5-ones

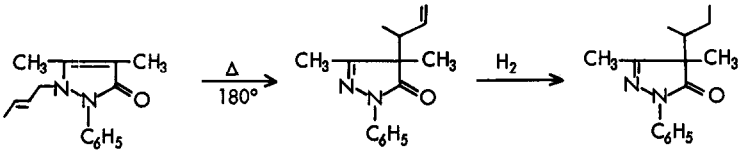
Compd. No.	$\nu_{max}^{CHCl_3}$ cm^{-1}			λ_{max}^{EtOH} mμ (log ε)
	C=O	-CH=CH$_2$		
Ia	1658	990	930	247(4.01) 275(3.96)
Ib	1660	991	916	247.5(4.00)276(4.01)
Ic	1652	962[a]		247(4.04) 275(3.99)
Id	1657	—		249.5(4.03)276.5(4.03)
IIa	1707	993	923	242(4.21)
IIb	1708	990	924	243(4.22)
IIc	1709	968[a]		242(4.23)
IId	1703	—		243(4.15)
III	1706	995	923	242(4.24)

a, The absorption band of the -CH=CH- group.

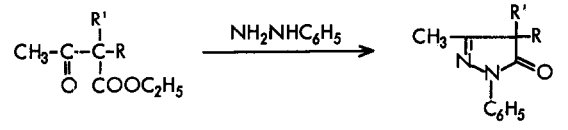
dimethyl-2-pyrazolin-5-one with crotyl chloride afforded 2-crotyl-1-phenyl-3,4-dimethyl-3-pyrazolin-5-one (Ic) as an oil (13) and 4-crotyl-1-phenyl-3,4-dimethyl-2-pyrazolin-5-one (IIc), b.$p_{0.07}$ 134-135° in the ratio of 1 to 2. Structures of these products were determined from the IR and UV spectral data (see Table I). Rearrangement of the N-2 crotyl compound Ic by heating at 180° for 30 min. afforded a quantitative yield of 4-(1-methylallyl)-1-phenyl-3,4-dimethyl-2-pyrazolin-5-one (III), b.$p_{0.3}$ 143-144°, with no detectable amount of IIc. A product obtained by catalytic hydrogenation of III over Pd-C was identical with 1-phenyl-4-sec-butyl-3,4-dimethyl-2-pyrazolin-5-one (IV), b.$p_{0.1}$ 128-129°, prepared by condensation of ethyl 2-acetyl-2,3-dimethylpentanoate with phenylhydrazine. Thus, it was confirmed that allyl migration from the N-2 to the C-4 in the pyrazolin-5-ones proceeds by a cyclic process with inversion of a migrating allyl group.

Comparing to the above amino-Claisen rearrangement, some similar alkyl migration reactions were attempted. Benzylation of 1-phenyl-3,4-dimethyl-2-pyrazolin-5-one gave 2-benzyl-1-phenyl-3,4-dimethyl-3-pyrazolin-5-one (Id), m.p. 132-133°, and 4-benzyl-1-phenyl-3,4-dimethyl-2-pyrazolin-5-one (IId), m.p. 83-84°. Although the N-2 benzyl compound Id did not rearrange at 180°, a 54% yield of the C-4 benzyl





Ic III IV



IIa-d, IV

a: R=CH_3, R'=$-CH_2CH=CH_2$ b: R=R'=$-CH_2CH=CH_2$

c: R=CH_3, R'=$-CH_2CH=CHCH_3$ d: R=CH_3, R'=$-CH_2C_6H_5$

compound IId together with a 37% recovery of the starting material were obtained on heating at 230° for 1.5 hr. The same treatment of 1-phenyl-2,3,4-trimethyl-3-pyrazolin-5-one resulted only in the recovery of the starting material.

A great facility of the allyl migration, when compared with the benzyl migration proceeding probably by an ionic cleavage-recombination mechanism, can be accommodated best by the assumption of a cyclic transition state.

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