Aromatic Aldehydes as Dienophiles

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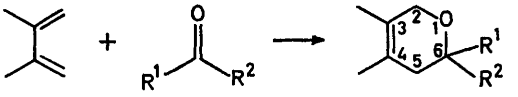
Summary The carbonyl group of aromatic aldehydes substituted in the benzene ring by electron-withdrawing groups may act as a dieneophile in a thermally induced cycloaddition reaction leading to dihydropyran derivatives; the same compounds and other dihydropyrans may also be obtained from dienes and these and other aromatic aldehydes by an alternative acid-catalysed reaction.

THE thermally induced reaction, (**1**) + (**2**) → (**3**), between conjugated dienes and substituted aldehydes and ketones to yield dihydropyran derivatives has been reported[1] to occur provided that the carbonyl component contains suitably placed electron-withdrawing groups. Thus the carbonyl component of the reaction may be an open-chain compound such as chloral (**2a**)[2] or carbonyl cyanide (**2b**)[3] or a cyclic compound such as *o*-chloranil (**4**)[4] or ninhydrin (**5**).[5]

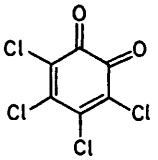
Formaldehyde[6] will also react in this way but the reaction with acetaldehyde although reported[2] to occur in low yield may be an acid-catalysed reaction. It has been stated[2] that the reaction does not occur with aromatic aldehydes including 4-nitrobenzaldehyde.



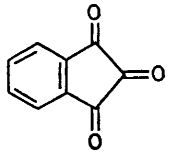
(1) (2) (3)

a; $R^1=H$, $R^2=CCl_3$
b; $R^1=CN$, $R^2=CN$
c; $R^1=4\text{-}NO_2C_6H_4$, $R^2=H$
d; $R^1=2\text{-}NO_2C_6H_4$, $R^2=H$
e; $R^1=2,4\text{-}(NO_2)_2C_6H_3$, $R^2=H$
f; $R^1=4\text{-}CNC_6H_4$, $R^2=H$
g; $R^1=H$, $R^2=H$
h; $R^1=4\text{-}ClC_6H_4$ $R^2=H$
i; $R^1=4\text{-}BrC_6H_4$, $R^2=H$
j; $R^1=4\text{-}FC_6H_4$, $R^2=H$
k; $R^1=4\text{-}MeOC_6H_4$, $R^2=H$

We now report that at 130° 4-nitrobenzaldehyde undergoes a thermally induced cycloaddition to dimethylbutadiene to give, in *ca.* 10% isolated yield, the dihydropyran (**3c**) m.p. 66—68°, δ 1·5—1·81 (6H, m, 3- and 4-Me), 2·05—2·32 (2H, m, 5-CH_2), 4·2 (2H, b.s, 2-CH_2), 4·66 (1H, t, *J* 6·5 Hz, 6-CH), 8·21, and 7·56 (4H, ABq, 9Hz, 6-Ar). Under essentially the same thermal conditions cycloaddition also occurs with 2-nitrobenzaldehyde to yield (**3d**) m.p. 70—71° (4%) and with 2,4-dinitrobenzaldehyde to yield (**3e**) m.p. 73—75° (11%). In these last two reactions considerable charring of the organic material was observed. However, with 4-cyanobenzaldehyde the adduct (**3f**) m.p. 102—104° is obtained in 32% yield.



(4)

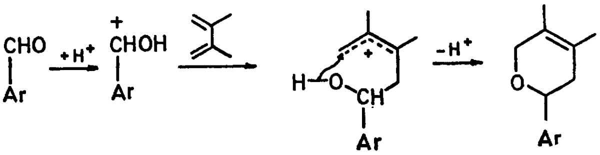


(5)

We have not been able to achieve a thermal reaction between dimethylbutadiene and benzaldehyde or its 4-chloro-, 4-bromo-, 4-fluoro-, or 4-methoxy-derivatives even at 130° for 24 h. However, these compounds react with dimethylbutadiene in the presence of toluene-4-sulphonic acid at *ca.* 80° to give the dihydropyrans (**3g**, **h**, **i**, **j**, and **k**) in yields of 50, 50, 35, 40, and 30%, respectively (estimated from g.l.c. analysis). The benzaldehydes containing electron-withdrawing groups also underwent the acid-catalysed reaction at 80° in the presence of toluene-*p*-sulphonic acid. In the absence of the acid catalyst no gas chromatographically detectable yields of dihydropyrans were obtained from these aldehydes even after 24 h at 80°.

We have considered the possibility that the higher temperature reactions may be acid-catalysed reactions, the acid being produced from the aldehyde. This would be consistent with the thermal reactions occurring only with those benzaldehydes containing electron-withdrawing groups as these would give rise to the stronger benzoic acids. If this were so then it would be expected that 4-cyanobenzoic acid would catalyse the addition of dimethylbutadiene to both benzaldehyde and anisaldehyde at 130°, the temperature at which 4-cyanobenzaldehyde and dimethylbutadiene react. However, when these experiments were carried out, no gas chromatographically detectable yield of dihydropyran was formed even after 24 h at 130°.

Our results clearly demonstrate that there are two distinct mechanisms for the formation of dihydropyrans from carbonyl compounds and conjugated dienes. The thermal reaction which is probably a concerted pericyclic reaction and the acid-catalysed reaction for which the rationalisation shown in the Scheme is suggested.



Scheme

All new compounds had spectroscopic and analytical data consistent with their assigned structures.

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