Flash Thermal Cyclization of 1-Arylbut-3-enyl Acetates

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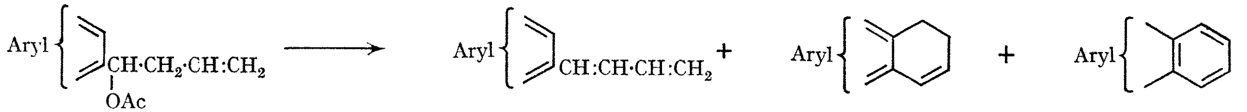
Summary When 1-arylbut-3-enyl acetates were flashed through a quartz tube at 500—900°, a Cope reaction occurred to give the cyclized compounds and in two cases unexpected isomerization was observed.

WHEN a solution of a 1-arylbut-3-enyl acetate (I)† in benzene was flashed through a quartz tube at 500—900°, elimination of acetic acid occurred to give the corresponding 1-arylbutadiene (II), as expected, together with its cyclized derivatives (III) and (IV). Reaction at higher temperatures (700—900°) gave a higher yield of (III) which was increasingly dehydrogenated with the elevation of the reaction temperature to give (IV). The cyclization is a peculiar type of Cope rearrangement where the aromatic ring acts as a 1,3,5-triene system (Table).

Pyrolysis of 1-*arylbut*-3-*enyl acetates*



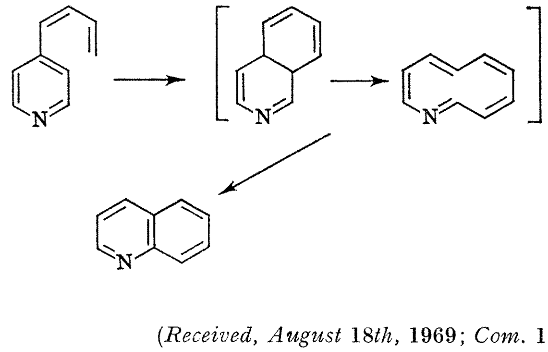
(I) (II) (III) (IV)

(I)	Pyrolysis temperature	(II)	Yield of product (%) (III)	(IV)	Unexpected product
Phenyl-	620°	—	30	60	—
Phenyl-	800	—	—	80	
2-Pyridyl-	550	30	20[a]	—	
2-Pyridyl-	670	—	30[a]	35	
4-Pyridyl-	620	—	55[b]	21	
4-Pyridyl-	830	—	—	40	20 (Quinoline)
2-Quinolyl-	670	20	30[c]	—	10 (Benzo[*f*]quinoline[d])
2-Furyl-	500	—	50[e]	4	6 (Phenylacetaldehyde)
2-Furyl-	600	—	—	18	42 (Phenylacetaldehyde)
2-Thienyl-	500	—	56[f]	4	
2-Thienyl-	600	—	—	41	

[a] 5,6-Dihydroquinoline: W. E. Hahn and T. Epsztjn, *Roczniki Chem.*, 1964, **38**, 964. Picrate m.p. 170° (from EtOH).
[b] 7,8-Dihydroisoquinoline. Picrate: m.p. 184—185° (from EtOH).
[c] 1,2-Dihydroacridine.
[d] I.r.: Identical with Sadtler Chart No. 7521.
[e] Mixture of 4,5-Dihydrobenzofuran and 6,7-dihydrobenzofuran. Treatment of the dihydrobenzofuran with sulphur, dichlorodicyanoquinone (DDQ), or *o*-chloranil gave benzofuran.
[f] Mixture of 4,5-dihydrobenzothiophen and 6,7-dihydrobenzothiophen. Dehydrogenation of dihydrobenzothiophens with DDQ or *o*-chloranil afforded benzothiophen in good yield.

Among the products, quinoline from 4-pyridylbut-3-enyl acetate and benzo[*f*]quinoline from 2-quinolylbut-3-enyl acetate were not expected. When isoquinoline was treated under the same conditions (830°), isomerization to quinoline occurred (*ca.* 10%). This percentage was far lower than that (33%) of thermal cyclization. No isomerization was observed on thermal treatment of acridine. This indicates that such types of isomerization are not possible in the thermal cyclization. A possible interpretation of this unusual reaction is that ten-membered-ring intermediates may be present before formation of quinoline.

Similar intermediates may be presumed precede the formation of benzo[*f*]quinoline.



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† Prepared from the corresponding arylaldehyde by means of Grignard's reaction with allyl chloride followed by acetylation.