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THE HOMOLYSIS OF REISSERT COMPOUNDS BY PHOTOLYTIC AND PEROXIDE-INDUCED PROCESSES

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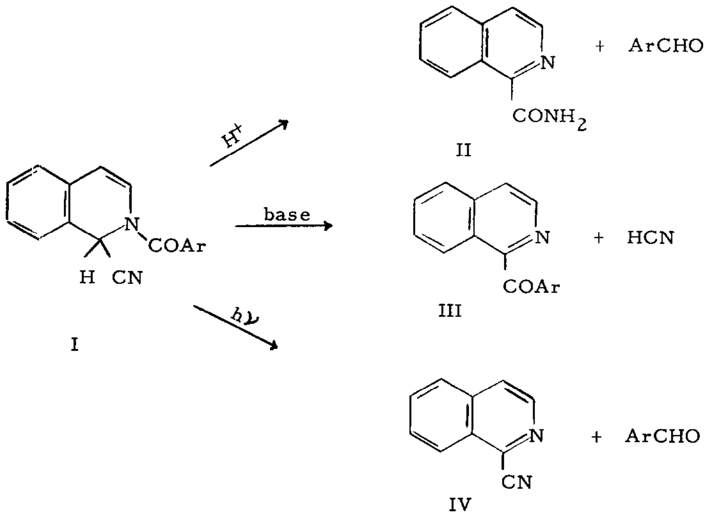
The acid-catalyzed decomposition of a Reissert compound such as I leads to an isoquinaldamide (II) and an aromatic aldehyde (1), while the base-catalyzed rearrangement of I results in loss of HCN to give a 1-aroylisoquinoline (III) (2). The mechanisms of these rearrangements have been studied by McEwen and his coworkers, who have demonstrated that the acid-catalyzed reaction does not proceed through the intermediacy of the nitrile (IV) (3).

We wish to report a novel photolysis of Reissert compounds, particularly evident in the isoquinoline series, which gives the nitrile (IV) as the principal product. For example, when 1-cyano-2-benzoyl-1,2-dihydroisoquinoline (Ia, Ar=C_6H_5) is irradiated with 2537 Å light in acetonitrile or t-butanol, 1-cyanoisoquinoline (IV) is produced in about 50% yield. In benzene solution, using a high-pressure mercury source, the yield of the nitrile (IV) was lower, while in isopropanol the photolysis yielded neither nitrile nor other recognizable products. In superficial analogy to the acid-catalyzed Reissert cleavage, the photolyses also produced the aldehydic fragment corresponding to the aroyl group, albeit in low yields. The fate of the major part of the aroyl fragment could not

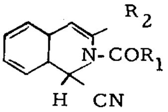


be determined. The experimental findings of typical photolyses in the isoquinoline Reissert series are summarized in Table I.

Photolyses in the Quinoline Series

Although the quinoline Reissert V, like its isoquinoline counterpart I, was also photolabile, the course of photolysis here showed a marked dependence on the wavelength of the ultraviolet source. Thus the action of a 2537 Å source on compound V in acetonitrile gave 2-cyanoisoquinoline (VI) in only 8% yield, plus a trace of benzaldehyde. With a high-pressure source and benzene as solvent there resulted instead 41% yield of a dimer(VII),(m.p. 323-324° dec.) as the only identifiable photoproduct. The data [Calcd. for $C_{34}H_{24}N_4O_2$: C, 78.4 H, 4.65; N, 10.76; M.W., 520.5. Found: C, 78.28; H, 4.72; N, 10.80; M.W., 517 (vapor pressure thermistor)] indicate that this substance involves "2+2" cycloaddition(4) of the styrene systems of two molecules

TABLE I

Reissert Compound(5) 	Solvent and Molar Concentration	Hours of Irradiation (a)	% Yield [b] of 1-cyanoisoquinoline	% Yield of Aromatic Aldehyde
I a, $R_1 = C_6H_5$	Acetonitrile(0.02)	19	47	5-14[c]
	Isopropanol(0.02)	24	0	0
b, R_1 = o-chloro-benzoyl	Acetonitrile(0.01)	19	71	
c, R_1 = 4-biphenyl-carbonyl	Acetonitrile(0.015)	23	30	12[d]
d, R_1 = 1-naphthoyl	Acetonitrile(0.016)	20	0	6[e]
e, R_1 = 3,4,5-trimethoxy benzoyl	Acetonitrile(0.014)	20	41	8[d]
	Benzene[f] (0.028)	20	34	12[d]
f, $R_1 = C_6H_5$ $R_2 = CH_3$	Acetonitrile(0.018)	24	15 (1-cyano-3-methyl-isoquinoline)	trace

a. The irradiations were carried out under an argon atmosphere using an ultraviolet source rich in 2537Å energy.

b. These were actual isolated yields obtained by silica gel chromatography and elution with 5% ethyl acetate - 95% benzene.

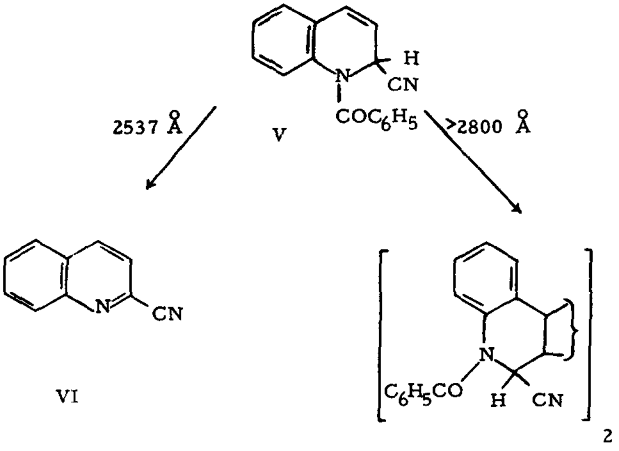
c. Determined by g. l. c.

d. Isolated by silica gel chromatography, elution with 5% ethyl acetate - 95% benzene and sublimation.

e. Isolated as the p-nitrophenylhydrazone.

f. A 200 watt high-pressure mercury lamp was used in this run.

of V, but neither the infrared (λ_{max}^{KBr} 6.04, 6.35, 6.70 and 6.90 μ), ultraviolet ($\lambda_{max}^{CH_3OH}$ 264 mμ, log ε 4.19) nor the n.m.r. spectrum (τ 2.50-2.83, multiplet, 18H; 3.88, singlet, 2H; A_2B_2 pattern at τ 6.38 and 6.75, 4H) permit a reasonable choice between the four possible isomers of the new cyclobutane system in VII.



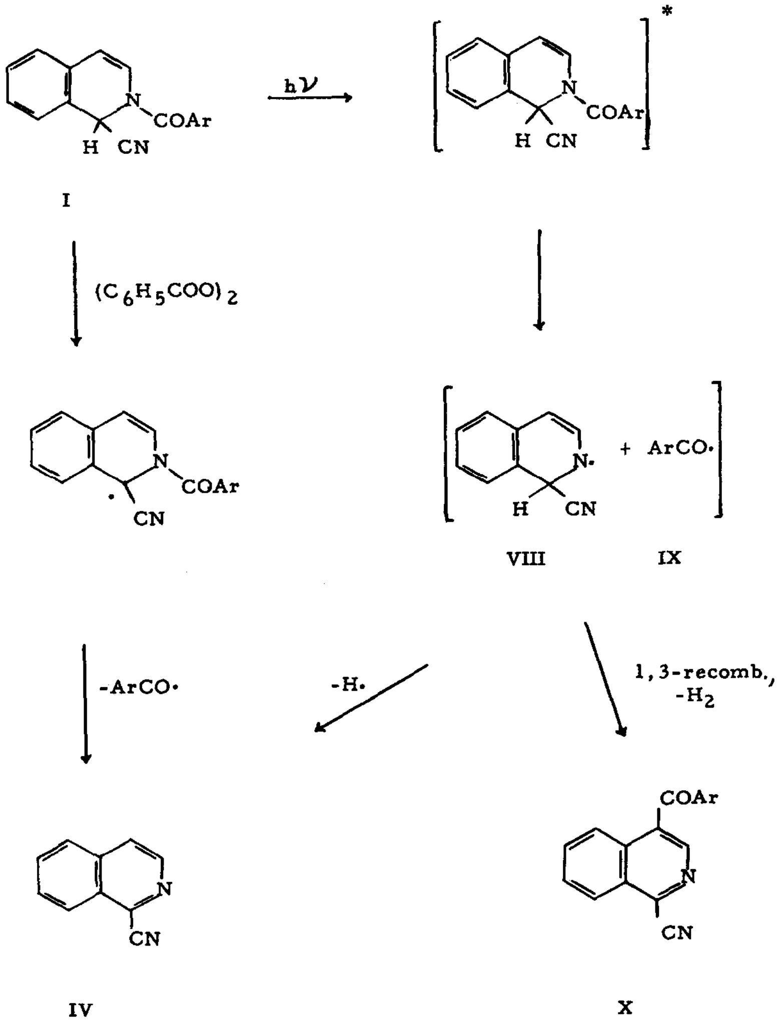
V

VI

VII

Peroxide-Induced Rearrangement

The blocking of the photoconversion I ⟶ IV by use of isopropanol solvent, as well as the striking difference in behavior between I and V, made it appear plausible that the formation of IV involved a free radical process. On this basis we examined the action of a radical initiator on assorted Reissert compounds. Indeed, treatment of the derivatives Ia(Ar = C_6H_5) and Ie(Ar = 3,4,5-$(OCH_3)_3$ C_6H_2) with an equimolar amount of benzoyl peroxide in boiling benzene gave


COAr
H CN
I
hν
*
COAr
H CN
(C6H5COO)2
COAr
CN
+ ArCO·
H CN
VIII
IX
-ArCO·
-H·
1,3-recomb.,
-H2
CN
IV
COAr
CN
X

1-cyanoisoquinoline (IV) in 30 and 52% yields, respectively; in contrast, the quinoline derivative V was essentially unchanged under the reaction conditions. This remarkable susceptibility of isoquinoline Reissert compounds to homolytic cleavage is, to our knowledge, without analogy.

It is premature to propose a precise mechanism to encompass the photochemical and peroxide-induced transformations leading to the nitriles. As a working hypothesis in the photolyses, however, one could envision N-C cleavage of an excited isoquinoline Reissert molecule to two radical fragments VIII and IX and subsequent H· transfer to the aroyl radical to give the principal product; the peroxide-induced reaction could presumably be initiated by H. transfer to C_6H_5COO. and subsequent N-C scission, a sequence essentially the inverse of the photochemical one. In regard to the photoactivated formation of the radical species VIII and IX, it is noteworthy that in photolyses of Ie (Ar= 3,4,5-$(OCH_3)_3$ C_6H_2) there is formed a byproduct, m.p. 188-190°, in 7% yield which gives all analytical [Calcd. for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.62, H. 4.83; N, 8.50] and spectroscopic data [λ_{max}^{KBr} 6.00, 6.30 μ; $\lambda_{max}^{CH_3OH}$ 330 mμ, log ε 4.05; n.m.r. includes a singlet at τ 1.27] consistent with the possible structure X (Ar=3,4,5-$(OCH_3)_3$ C_6H_2), a species which could arise by allylic recombination of the postulated fragments VIII and IX and subsequent aromatization.

References

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4. For example, see G. S. Hammond, C. A. Stout, and A. A. Lamola, J. Am. Chem. Soc., 86, 3103 (1964), and references cited therein.
5. All the Reissert compounds were prepared according to the method described by F. Popp, W. Blount, and P. Melvin, J. Org. Chem., 26, 4930 (1961).