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THERMAL REARRANGEMENT OF ALLYL 2-QUINOLYL ETHERS

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A number of studies have established that a great deal of specificity is observed in the direction of Claisen rearrangement and this specificity has been interpreted on the basis of bond structure (1) or electronic structure (2) of the parent aromatic nucleus. Our previous works (3, 4) on the thermal rearrangement of allyl 2,3-disubstituted 4-quinolyl ethers suggested a possibility of the Claisen rearrangement to the ring nitrogen. In this work allyl 2-quinolyl ethers possessing two dissimilar ortho positions were chosen as the reaction system of thermal rearrangement.

Heating 2-allyloxyquinoline (Ia), b.$p_{0.25}$ 107-108°; picrate, m.p. 144-145°, prepared from 2-chloroquinoline and sodium allyloxide by Tschitschibabin's method (5), at 250° for 1 hr. without solvent resulted in the formation of a 17.8% yield of 1-allylcarbostyril (IIa), b.$p_{0.45}$ 144-145°; $\nu_{C=O}^{CHCl_3}$ 1655 cm^{-1}, and in the recovery (77%) of Ia. Rearrangement of Ia at 300° for 1 hr. afforded two isomeric products: IIa in 48.8% yield and 1-propenylcarbostyril (IIIa), b.$p_{0.1}$ 123-124°; $\nu_{C=O}^{CHCl_3}$ 1650 cm^{-1}, in 37.6% yield along with a 0.8% yield of carbostyril (IV).

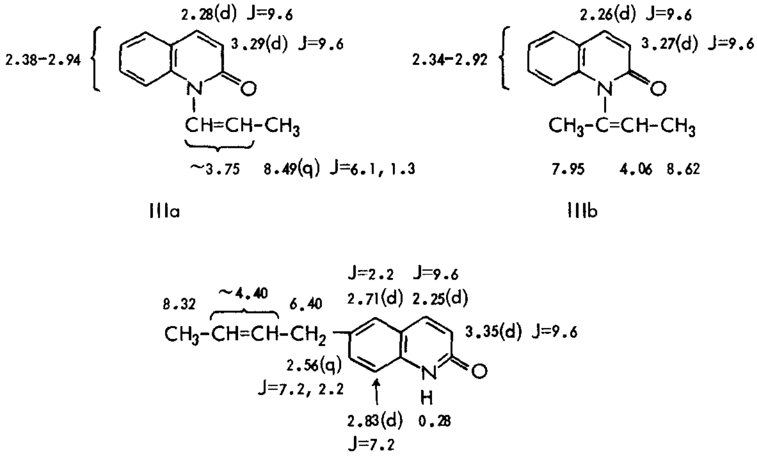
Heating 2-crotyloxyquinoline (Ib), b.$p_{1.0}$ 115-116°; picrate, m.p. 111-112°, prepared by the reaction of 2-chloroquinoline and sodium crotyloxide, at 250° for 1 hr. gave a 20.3% yield of 1-(1-methylallyl)-carbostyril (IIb), b.$p_{0.5}$ 144-145°;

$\nu_{max}^{CHCl_3}$ 1657 (C=O) and 993 and 920 (CH=CH$_2$) cm^{-1}, with a 72.5% recovery of Ib. Analogous rearrangement of Ib at 300° for 1 hr. afforded three isomeric products: IIb in 36.8% yield, 1-(1-methylpropenyl)-carbostyril (IIIb), b.p$_{0.01}$ 120-121°; $\nu_{C=O}^{CHCl_3}$ 1657 cm^{-1}, in 30.7% yield, and 6-crotylcarbostyril (Vb), m.p. 149-150°; ν_{max}^{Nujol} 3171 (NH), 1663 (C=O), and 974 (CH=CH) cm^{-1}, in 1.0% yield along with a 14.2% yield of IV.

The structure of these rearrangement products was confirmed by the following spectral analyses and chemical results. All the products showed ultraviolet absorption curves characteristic for the carbostyril nucleus. IIa was identical with an authentic sample of 1-allylcarbostyril (5) obtained by alkylation of the sodium salt of IV with allyl bromide. Alkylation of sodium salt of IV with propyl bromide in boiling ethanol for 5 hrs. afforded 1-propylcarbostyril (VIa), b.p$_{0.3}$ 129-130°; $\nu_{C=O}^{CHCl_3}$ 1652 cm^{-1}, and 2-propyloxyquinoline (VIIa), b.p$_{0.3}$ 93-94°, in the ratio of about 2 : 1. Similar reaction of sodium salt of IV with *sec*-butyl bromide gave 1-*sec*-butylcarbostyril (VIb), b.p$_{0.15}$ 118-119°; $\nu_{C=O}^{CHCl_3}$ 1652 cm^{-1}, and 2-*sec*-butyloxyquinoline (VIIb), b.p$_{0.7}$ 107-108°, in the ratio of 1 : 2. Catalytic hydrogenation of IIIa over PtO$_2$ in ethanol yielded a colorless oil, identical with VIa by infrared spectral comparison. Analogously, catalytic hydrogenations of IIb over Pd-c and IIIb over PtO$_2$ gave the same reduction product, which was identical with VIb by infrared spectrum comparison. The n.m.r. spectra of IIIa and IIIb exhibited the signals supporting the above assigned structures as shown in Fig. 1. The structure of Vb was reasonably assigned to 6-crotylcarbostyril from the infrared, ultraviolet and n.m.r. spectral results. As shown in Fig. 1, Vb exhibited the three proton signals (*meta*-coupling proton, *ortho*- and *meta*-couplings proton and *ortho*-coupling proton) at 2.71, 2.56, and 2.83 τ respectively corresponding to the H$_5$,

FIG. 1

N.m.r. Spectral Data* (chemical shift: τ, J: c.p.s.)



IIIa

IIIb

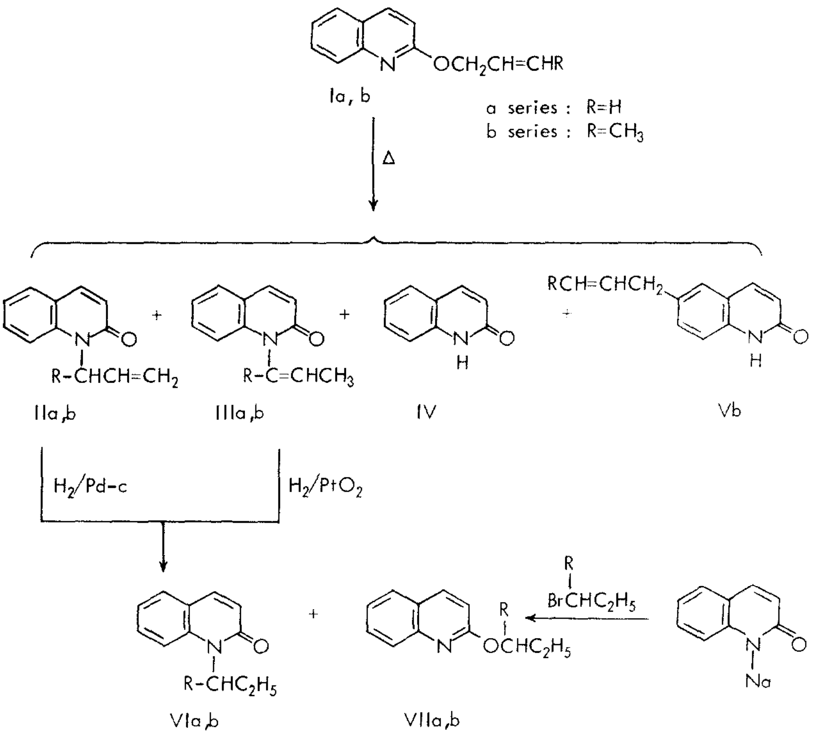
Vb

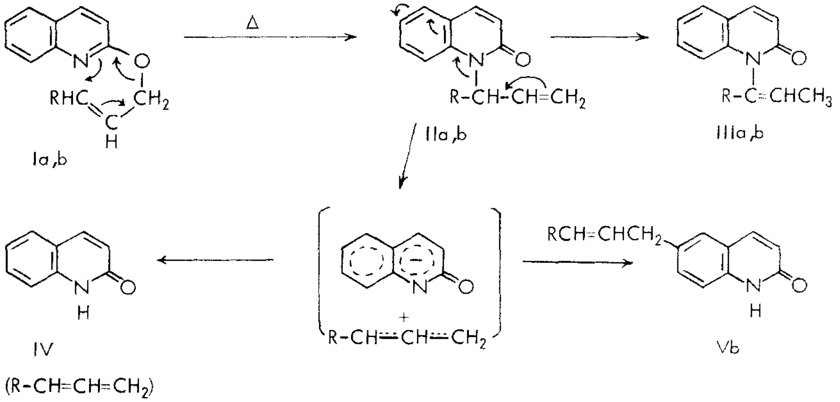
* The spectra were observed on deuteriochloroform solution containing tetramethylsilane as an internal standard by using a Varian A-60 Spectrometer.

H_7, and H_8 as the ring protons of the benzene-ring part.

Thus, it was evident that the ortho-Claisen rearrangement of allyl 2-quinolyl ethers proceeds to only the ring nitrogen in two ortho-positions. Since Dinan and Tieckelmann (6) very recently reported the interesting result that the ortho-Claisen rearrangement of allyl 2-pyridyl ethers proceeds to the N-1 and C-3 to nearly the same extent, our result demonstrates that the direction of the Claisen rearrangement of allyl 2-quinolyl ethers is towards a napthoid activity.

On the other hand, it was confirmed that the by-products (IIIa,b, IV, and


Ia, b
OCH₂CH=CHR
a series : R=H
b series : R=CH₃
Δ
IIa,b
IIIa,b
IV
Vb
R-CHCH=CH₂
R-C=CHCH₃
RCH=CHCH₂
H₂/Pd-c
H₂/PtO₂
R-CHC₂H₅
OCHC₂H₅
BrCHC₂H₅
Na
VIa,b
VIIa,b


Ia,b
Δ
RHC
CH₂
IIa,b
R-CH-CH=CH₂
IIIa,b
R-C=CHCH₃
R-CH⋯CH⋯CH₂
RCH=CHCH₂
IV
(R-CH=CH=CH₂)
Vb

Vb) in the rearrangement reaction of Ia,b at 300°, were produced by the consecutive transformation of the Claisen rearrangement products (IIa,b) in the process of rearrangement of Ia,b. Namely, treatment of IIa under the rearrangement conditions (at 300°) resulted in the formation of 44.6% of IIIa and 1.4% of IV with the recovery of 37.9% of IIa. Analogous treatment of IIb afforded 38.4% of IIIb, 12.5% of IV, and 1.2% of Vb along with the recovery of 32.9% of IIa.

These by-products in the Claisen rearrangement would be produced by the following pathways. The Claisen products (IIa,b) were transformed to the thermodynamically stable form by double bond shift to give IIIa,b. A part of IIa,b was converted to ion-pair as an intermediate and alternatives may ensue following ionization. Dissociation could yield carbostyril (IV), a product always found in these reactions, and allene derivatives. Ion-pair collapse and alkylation with crotyl cation would give 6-crotylcarbostyril (Vb). As a 1-methylallyl cation is stabilized by the I-effect of the methyl group, in comparison with an allyl cation, a relatively large amount of carbostyril (IV) and Vb would be produced from IIb.

For all the compounds described, satisfactory elemental analyses were obtained.

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