Anal. Calcd. for $C_{16}H_{17}NO \cdot C_6H_3N_3O_7$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.39; H, 4.38; N, 12.03.

Elution with chloroform afforded 1.39 g. (58.2%) of IVf as colorless plates, m.p. 72–73°, on recrystallization from benzene–petroleum ether: ν_{max} 1630 (C=O), 984, 927 (—CH=CH_3), and 895 (>C=CH_2) cm.$^{-1}$. The ultraviolet spectrum showed the 4(1H)-quinolone nucleus (Table I). The n.m.r. spectrum showed singlets at τ 8.24 (CH_3) and 6.67 (CH_2 at C-3).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.14; H, 7.36; N, 5.89.

Rearrangement of 4-Allyloxy-3-propylquinoline (IIIa).—The allyl ether IIIa (200 mg.) was heated without solvent at 200° for 30 min. Thin layer chromatography of the reaction product on an alumina plate showed a single spot, indicating an identical R_f value with that of IVa. Chromatography on alumina afforded 192 mg. (96%) of a colorless oil, which had an infrared spectrum identical with that of IVa, and no other product was detectable. The picrate had m.p. 115–116° and showed no depression of the melting point on admixture with the picrate of IVa.

Rearrangement of 4-Crotyloxy-3-propylquinoline (IIIb).—The rearrangement of 300 mg. of IIIb was conducted at 200° for 30 min. The composition of the reaction mixture was investigated by thin layer chromatography and a single spot, identical with that of IVb, appeared. Careful chromatography on alumina gave 290 mg. (97%) of a colorless oil, identical with IVb by infrared spectrum, and any other product was not detectable. The picrate had m.p. 128–129° and showed no depression of melting point on admixture with that of IVb.

Rearrangement of 3-Allyl-4-crotyloxyquinoline (IIIc).—The crotyl ether IIIc (600 mg.) was heated without solvent at 200° for 30 min. The composition of the reaction mixture was investigated by thin layer chromatography and a single spot, indicating an identical R_f value with that of IVc, appeared. Chromatography on alumina gave 570 mg. (95%) of a colorless oil, identical with IVc by infrared spectrum, and any amount of IVd was not detectable.

Rearrangment of 4-Allyloxy-3-(1-methylallyl)quinoline (IIId).—The rearrangement of 300 mg. of IIId was examined by the same method as that for IIIc. An almost quantitative amount of IVc and no detectable amounts of IVd were obtained.

Rearrangement of 3-Allyl-4-methallyloxyquinoline (IIIe).—The methallyl ether IIIe (500 mg.) was heated without solvent at 200° for 30 min. After cooling, the reaction mixture was dissolved in chloroform and chromatographed on alumina. Gradient elution with benzene, chloroform, and ethyl acetate gave 480 mg. of a semisolidified product. A typical analysis of this product is given below.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.38; H, 7.19; N, 5.86.

The infrared spectrum of the product was identical with that of a mixture (about 1:1) of the two pure 4(1H)-quinolones IVe and IVf. The n.m.r. spectrum showed signals corresponding to those of a mixture of IVe and IVf.

Rearrangement of 4-Allyloxy-3-methallylquinoline (IIIf).—The rearrangement of 400 mg. of IIIf was conducted in the same way as for IIIe described above. There was obtained 380 mg. of the 4(1H)-quinolone product, which was completely identical with that obtained from IIIe by infrared and n.m.r. spectra.

Computation of the Compositions of the Rearrangement Products from the N.m.r. Spectra.—Compositions of the product obtained from IIIe were calculated from n.m.r. spectra of 10% solutions of the unknowns and the two pure 4(1H)-quinolones IVe and IVf in deuteriochloroform. The proton signals of the CH_2 group at τ 6.54 and 6.67 were used. The product was determined to be a mixture of IVe and IVf in the proportion of about 1:1 on the basis of the relative integrated intensities of both signals. The product obtained from IIIf showed proton signals of the same proportion of IVe and IVf as those of the product from IIIe in n.m.r. spectrum.

Acknowledgment.—The author is sincerely grateful to Professor E. Ochiai, Dr. K. Takeda, and Dr. H. Kano for their encouragement, and to Dr. H. Tanida for his helpful discussions.

The Claisen Rearrangement. IV.[1] "Out-of-Ring" Claisen Rearrangement to the Active Methylene Group of a *meta* Side Chain in Allyl 4-Quinolyl Ethers[2]

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Received November 17, 1964

Thermal rearrangement of allyl 2,3-dialkyl-4-quinolyl ethers (Ia–c) affords good yields of the corresponding 2-(3-butenyl)-4(1H)-quinolones (IIa–c) formed by attachment of the allyl group to the active methylene group at C-2, along with small amounts of 1-allyl-2,3-dialkyl-4(1H)-quinolones (IIIa–c) and the tricyclic compounds (IVa–c) formed by the intramolecular ring closure of the former products (IIa–c). The formation of IIa–c is explicable by a sequence of two consecutive cyclic transition states, the last of which involves a tautomerism of the imine–enamine variety.

The Claisen rearrangement maintains importance among organic reactions as an excellent prototype of a thermally induced, intramolecular isomerization.[3]

In 1926, Claisen and Tietze[4] reported a second type of rearrangement of substituted phenyl allyl ethers. Unlike the then known rearrangements of allyl phenyl ethers in which the migrating allyl group eventually becomes attached directly to the aromatic nucleus, this rearrangement proceeds in such manner that the allyl residue becomes attached, not to the benzene ring, but to the β-carbon of an *o*-propenyl side chain.[5]

It has been demonstrated that the *para* Claisen rearrangement yields products which are consistent with the proposal of Hurd and Pollack[6] involving a double inversion and results suggest that this rearrangement proceeds through a dienone intermediate. An interesting similarity of a mechanism of the rearrangement of an allyl residue to an *o*-propenyl side chain to that of the *para* Claisen rearrangement was reported by Lauer[7] and Schmid.[8]

(1) Part III: Y. Makisumi, *J. Org. Chem.*, **30**, 1986 (1965).

(2) A preliminary report of this work was published in *Tetrahedron Letters*, **No. 13**, 699 (1964).

(3) For an excellent recent review of the Claisen rearrangement, see S. J. Rhoads, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y. 1963, p. 655.

(4) L. Claisen and E. Tietze, *Ann.*, **449**, 81 (1926).

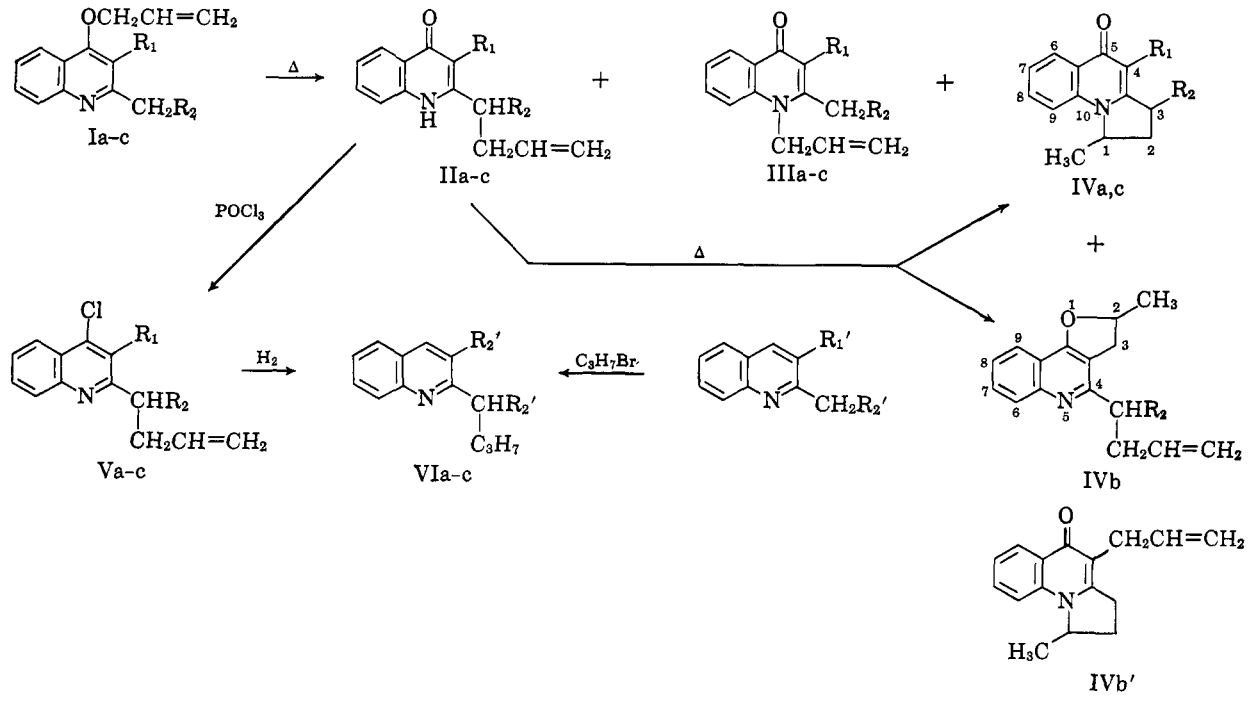
(5) It should be noted that Nickon observed the allyl migration to the β-carbon of a *p*-propenyl side chain [see A. Nickon and B. R. Aaronoff, *J. Org. Chem.*, **27**, 3379 (1962); **29**, 3014 (1964)].

(6) C. D. Hurd and M. A. Pollack, *ibid.*, **3**, 550 (1939).

(7) W. M. Lauer and D. M. Wujciak, *J. Am. Chem. Soc.*, **78**, 5601 (1956).

(8) K. Schmid, P. Fahrini, and H. Schmid, *Helv. Chim. Acta*, **39**, 708 (1956).

CHART I



a, $R_1 = R_1' = CH_3$; $R_2 = R_2' = H$
b, $R_1 = -CH_2CH=CH_2$; $R_1' = C_3H_7$; $R_2 = R_2' = H$
c, $R_1 = R_1' = CH_3$; $R_2 = -CH_2CH=CH_2$; $R_2' = C_3H_7$

Recently, the author[9] reported that the allyl group of 7-allyloxy-5,6-dimethyl-*s*-triazolo[1,5-*a*]pyrimidine migrates to the active methyl group at the 5-position (*meta* position to the ether group) by its intramolecular rearrangement and that this rearrangement can be elucidated by a similar mechanism to that of the *para* Claisen rearrangement. Accordingly, this migration of an allyl group to the active methylene group of a *meta* side chain is very interesting as an extension of the Claisen rearrangement.

In the present work, thermal rearrangement of 3-substituted 2-alkyl-4-quinolyl allyl ethers is investigated in order to extend this new type of Claisen rearrangement to the quinoline ring system (see Chart I).

Mandel-Jones and Trikojus[10] have reported that the thermal rearrangement of 4-allyloxy-2,3-dimethylquinoline (Ia) gives a substance of m.p. 250° to which they have assigned 5-allyl-2,3-dimethyl-4-quinolinol. However, the structure of this product would be expected to be 2-(3-butenyl)-3-methyl-4(1H)-quinolone formed by the migration of the allyl group to the methyl group at C-2 from the point of view of our new type of Claisen rearrangement. Therefore, the thermal rearrangement of the allyl ether Ia was at first investigated.

When the allyl ether Ia was heated without solvent at 200° for 30 min., there was obtained a 92% yield of an isomeric product (IIa), m.p. 260–261°, as benzene-insoluble crystals after treatment of the reaction mixture with benzene. The ultraviolet spectrum of IIa shows an absorption curve characteristic for the 4(1H)-quinolone nucleus[1] as shown in Table I and the infrared spectrum exhibits absorption bands of NH, lactam C=O, and $-CH=CH_2$. Reaction of IIa with phosphorus oxychloride yielded the corresponding 4-chloro derivative Va which exhibits one singlet methyl (τ 7.48) and a complex multiplet (τ 1.8–2.7) due to four aromatic protons in the n.m.r. spectrum. Va was further converted into alkylquinoline VIa by catalytic hydrogenation over palladium on carbon and sodium acetate, after absorption of 2 molar equiv. of hydrogen. The infrared spectrum of VIa was identical with that of 2-butyl-3-methylquinoline synthesized from 2,3-dimethylquinoline by an unequivocal method[11]: propylation with propyl bromide in liquid ammonia in the presence of sodamide. A mixture melting point of the picrates of both samples gave no depression. The structure of the rearrangement product IIa was thus proved to be not the 5-allyl compound which was proposed by Mandel-Jones and Trikojus, but the expected 2-(3-butenyl)-3-methyl-4(1H)-quinolone.

Similarly, 4-allyloxy-3-allyl-2-methylquinoline (Ib) was prepared by the reaction of 3-allyl-2-methyl-4-quinolinol[12] with allyl bromide in the presence of a base and rearranged under the same conditions as for Ia. A rearrangement product, 3-allyl-2-(3-butenyl)-4(1H)-quinolone (IIb), m.p. 243–244°, as benzene-insoluble crystals, was isolated in a 90.4% yield. The infrared and ultraviolet spectra were consistent with the proposed structure. Chlorination of IIb with phosphorus oxychloride gave the corresponding 4-chloro derivative Vb which shows no proton signal attributed to a methyl group in the n.m.r. spectrum. Catalytic reduction of Vb afforded alkylquinoline VIb, b.p. 136–138° at 0.2 mm., which was identical

(9) Y. Makisumi, *Chem. Pharm. Bull.* (Tokyo), **11**, 859 (1963).

(10) B. Mandel-Jones and W. M. Trikojus, *J. Proc. Roy. Soc. N. S. Wales*, **66**, 300 (1932).

(11) It has been known that an active methylene group at the 2- or 4-position of pyridine and quinoline is readily alkylated by the action of alkyl halide in liquid ammonia in the presence of sodamide [see F. W. Bergstrom, *J. Am. Chem. Soc.*, **53**, 3027, 4065 (1931); F. W. Bergstrom, T. R. Norton, and R. A. Seibert, *J. Org. Chem.*, **10**, 452 (1945)].

(12) Y. Makisumi, *Chem. Pharm. Bull.* (Tokyo) **12**, 789 (1964).

TABLE I

ULTRAVIOLET SPECTRA OF THE REARRANGEMENT PRODUCTS

Compd.	λ_{max}, mμ (log ε)							
IIa	213 (4.45)	240 (4.51)	246.5 (4.50)	282.5 (3.31)[a]	294 (3.47)[a]	323 (4.09)	336 (4.11)	
IIb	213 (4.43)	241 (4.49)	248 (4.49)	282 (3.36)[a]	294 (3.50)[a]	322.5 (4.06)	335.5 (4.08)	
IIc	213 (4.47)	241 (4.53)	246.5 (4.53)	282.5 (3.30)[a]	294 (3.42)[a]	324 (4.10)	337.5 (4.14)	
IIIa	214 (4.40)	242.5 (4.44)	249 (4.42)	282 (3.23)[a]	293.5 (3.33)[a]	329 (3.12)	342 (4.16)	
IIIb	213 (4.38)	242 (4.44)	250 (4.40)	281 (3.23)[a]	292.5 (3.31)[a]	329 (4.14)	342.5 (4.18)	
IIIc	215.5 (4.35)	244 (4.47)	251 (4.45)	282.5 (3.22)[a]	294 (3.37)[a]	331 (4.13)	345.5 (4.20)	
IVa	213 (4.45)	242.5 (4.43)	248.5 (4.44)	284 (3.30)[a]	295 (3.44)[a]	328.5 (4.10)	341 (4.13)	
IVc	214 (4.46)	243 (4.46)	250 (4.47)	284 (3.29)[a]	295.5 (3.43)[a]	329 (4.10)	341.5 (4.13)	
IVb	214 (4.45)[a]	230.5 (4.74)	286 (3.74)[a]	292.5 (3.79)	303 (3.70)[a]	310 (3.57)[a]	316.5 (3.41)[a]	

[a] Shoulder.

with 2-butyl-3-propylquinoline prepared by the propylation[11] of 2-methyl-3-propylquinoline[13] (VII).

Since it became thus evident that the migration of an allyl group to the active methyl group at C-2 does readily proceed in the thermal rearrangement of 3-substituted 2-methyl-4-quinolyl allyl ethers, an attempt of a similar migration reaction of an allyl group to the α active methylene of a *meta* side chain was undertaken.

As the starting material, 4-allyloxy-2-(3-butenyl)-3-methylquinoline (Ic) was prepared by the action of allyl bromide on IIa in the presence of a base. Thermal rearrangement of Ic under the same conditions as for Ia resulted in the formation of a rearrangement product (IIc), m.p. 239–240°, in a 90% yield. IIc shows a very similar absorption to that of IIa in the ultraviolet spectrum (see Table I) and exhibits absorption bands of the NH, lactam C=O, and —CH=CH_2 groups in the infrared spectrum. Chlorination of IIc with phosphorus oxychloride gave the corresponding 4-chloro derivative Vc, b.p. 127–128° at 0.15 mm., which exhibits a singlet methyl (τ 7.43) and a complex multiplet (τ 1.7–2.7) due to four aromatic protons. Catalytic reduction of Vc afforded alkylquinoline VIc, b.p. 126–127° at 0.15 mm. The infrared spectrum of VIc was identical with that of 2-(1-propylbutyl)-3-methylquinoline synthesized by the propylation[11] of VIa, and a mixture melting point of the picrates of both samples was not depressed. Therefore, the structure of the rearrangement product (IIc) was established to be 2-(1-allyl-3-butenyl)-3-methyl-4(1H)-quinolone formed by the migration of the allyl group to the α-carbon of the *meta* side chain.

Thus, the new type of "out-of-ring" Claisen rearrangement to the α-carbon of a *meta* side chain was successfully extended to the quinoline derivative.

The above rearrangement of allyl 2,3-dialkyl-4-quinolyl ethers resulted in the formation of about 90% of the product, in which the allyl group had migrated to the α-carbon of the *meta* side chain, as benzene-insoluble crystals. To determine the composition of the remainder of the reaction mixture, the residue (the benzene-soluble part) from the rearrangement of the allyl ethers Ia–c was investigated.

Each of the benzene-soluble parts of the reaction mixtures was chromatographed on alumina and two kinds of products, N-allyl-4(1H)-quinolones IIIa–c and the tricyclic compounds IVa–c, isomeric to the starting material, were isolated, respectively. The ultraviolet spectra of IIIa–c show absorption shapes characteristic for the 4(1H)-quinolone nucleus as shown in Table I, and the infrared spectra exhibit strong absorption bands (1620–1625 $cm.^{-1}$) due to the carbonyl stretching[1,14] of 1-alkyl-4(1H)-quinolones and lack those due to the NH stretching. It would therefore be reasonable to propose the 1-allyl-4(1H)-quinolone structure formation by the migration of the allyl group to the ring nitrogen for IIIa–c. The n.m.r. spectra[15] of these products (IIIa–c) substantiate the structure proposed above. From these results, it was determined that IIIa is 1-allyl-2,3-dimethyl-4(1H)-quinolone, IIIb is 1,3-diallyl-2-methyl-4(1H)-quinolone, and IIIc is 1-allyl-2-(3-butenyl)-3-methyl-4(1H)-quinolone.

The ultraviolet spectra of IVa and IVc are very similar to those of the 1-allyl-4(1H)-quinolones (IIIa–c) and their infrared spectra show the presence of the carbonyl group corresponding to that[1,14] of the 1-alkyl-4(1H)-quinolones and the absence of the NH group and the double bond of the side chain. These spectral analyses suggest that IVa and IVc should be the 2,3-dihydropyrrolo[1,2-*a*]quinolin-5(1H)-one derivatives formed by an intramolecular cyclization between the ring nitrogen and the double-bond carbon in IIa and IIc, respectively. The n.m.r. spectral analysis shows that IVa and IVc, respectively, are 1,4-dimethyl-2,3-dihydropyrrolo[1,2-*a*]quinolin-5(1H)-one and its 3-allyl derivative. Then an intramolecular cyclization reaction of IIa and IIc was attempted. Heating IIa with zinc chloride at over 200° afforded the expected ring-closure compound, 1,4-dimethyl-2,3-dihydropyrrolo[1,2-*a*]quinolin-5(1H)-one, which was identical with IVa obtained from the rearrangement of Ia by mixture melting point determination and infrared spectral comparison. Similarly, IVc was also proved to be identical with 3-allyl-1,4-dimethyl-2,3-dihydropyrrolo[1,2-*a*]quinolin-5(1H)-one prepared by the intramolecular cyclization of IIc. The last compound IVb,

(13) This compound was prepared from 3-allyl-2-methyl-4-quinolinol by chlorination with phosphorus oxychloride followed by catalytic reduction over palladium on carbon.

(14) It has been reported that the carbonyl absorption in the 1-alkyl-4(1H)-quinolones appear at around 1620 $cm.^{-1}$ [see H. Rapoport and K. G. Holdon, *J. Am. Chem. Soc.*, **82**, 4395 (1960)].

(15) The proton signal due to H-5 appears in a relatively low field in comparison with the signals of other aromatic protons in these n.m.r. spectra. Goodwin, *et al.*,[16] have demonstrated that H-5 is considerably deshielded as compared with the other ring protons by the carbonyl group at C-4 in the n.m.r. spectra of the 4(1H)-quinolones. In a survey of the n.m.r. spectra of furoquinoline alkaloids possessing a 1-alkyl-4(1H)-quinolone skeleton, Robertson, *et al.*,[17] also have reported that the signal from one of the aromatic protons was almost always at a noticeably lower field (*ca.* 60 c.p.s.) than the other aromatic signals and they have assigned the low-field proton as H-5.

(16) S. Goodwin, J. N. Schoolery, and L. F. Johnson, *J. Am. Chem. Soc.*, **81**, 3065 (1959).

(17) A. V. Robertson, *Australian J. Chem.*, **16**, 451 (1963); J. A. Bosson, M. Rasmussen, E. Ritchie, A. R. Robertson, and W. C. Taylor, *ibid.*, **16**, 480 (1963).

obtained from the rearrangement of Ib, shows the presence of the ether linkage and the absence of the C=O and NH groups in the infrared spectrum and an absorption curve corresponding to that[12] of the 2,3-dihydrofuro[3,2-*c*]quinolines in the ultraviolet spectrum. Thus, the structure of IVb was assigned to 4-(3-butenyl)-2-methyl-2,3-dihydrofuro[3,2-*c*]quinoline which is probably formed by the ring closure of IIb. This assigned structure was supported by the n.m.r. spectrum. Then 4-(3-butenyl)-2-methyl-2,3-dihydrofuro[3,2-*c*]quinoline was prepared by the heating of IIb with pyridine hydrochloride according to the method of the previous work,[12] and the identity of this compound and IVb was proved by mixture melting point and comparison of their infrared spectra. Heating of IIb with zinc chloride at over 200° resulted in the formation of IVb. The same type of ring-closure product (IVb′) as the 2,3-dihydropyrrolo[1,2-*a*]quinolin-5(1H)-one derivative, obtained by the pyrolysis of IIa or IIc, was not detectable.

Thus, it was evident that the thermal rearrangement of allyl 2,3-dialkyl-4-quinolyl ethers results in the formation of two types of rearrangement products formed by the migration of the allyl group to the α-carbon of the *meta* side chain and to the ring nitrogen, and some parts of the former products are consecutively transformed by their intramolecular cyclization into the tricyclic compounds in the course of this rearrangement reaction.

In order to determine whether both types of rearrangements proceed competitively or consecutively, the C-allyl compounds, IIa–c, and the N-allyl compounds, IIIa–c, were subjected to the rearrangement conditions. Careful investigation of the reaction mixture failed to reveal the presence of any of the transformed compounds, except the cyclization compounds, IVa–c, from the C-allyl compounds. Namely, heating of the C-allyl compounds at 200° for 30 min. without solvent resulted in the recovery of over 90% of the starting materials and the formation of a few per cent of the cyclization compounds. No detectable amounts of the N-allyl compounds were formed. On the other hand, treatment of the N-allyl compounds under the same conditions as for the C-allyl compounds resulted in the recovery of almost quantitative amounts of the starting materials and the C-allyl compounds were not detectable.

These results rule out the possible existence of a consecutive pathway between both types of rearrangement products and demonstrate the formation of IIa–c and IIIa–c from the allyl ethers, Ia–c, as a result of competitive rearrangements of the allyl group from the oxygen to the α-carbon of the *meta* side chain and the ring nitrogen.

Since it has been established in the preceding work[1] that the migration of an allyl group to the *para* ring nitrogen is a Claisen rearrangement, it should be considered that both types of rearrangement reported here proceed by a mechanism involving a double inversion of a migrating allyl group *via* the same dienone-type intermediate and compete in the second six-membered cyclic stages having a different orientation of the migrating allyl group. The second cyclic stage in the rearrangement to the side chain is explicable in consideration of a tautomerism of the imine–enamine variety.

Experimental

Boiling points are uncorrected. Melting points were determined using a Kofler hot stage and are uncorrected. The infrared spectra were recorded in chloroform solution unless otherwise specified and the ultraviolet spectra were run in 95% ethanol solution. The n.m.r. spectra were obtained in deuteriochloroform solution with a Varian A-60 spectrometer, using tetramethylsilane as an internal standard.

General Procedure for the Preparation of the Allyl 4-Quinolyl Ethers (Ia–c). Synthesis of Ia. A.—Ia was prepared from 5.6 g. (0.02 mole) of the silver salt of 2,3-dimethyl-4-quinolinol and 2.66 g. (0.022 mole) of allyl bromide in 40 ml. of absolute ethanol according to the method of Mandel-Jones.[10] Distillation of the oily product gave 1.96 g. (46%) of Ia as a colorless oil, b.p. 120–121° (0.15 mm.).

B.—To a boiling suspension of 5.2 g. (0.03 mole) of 2,3-dimethyl-4-quinolinol and 4.5 g. (0.033 mole) of the powdered potassium carbonate in 70 ml. of anhydrous acetone was added 4.0 g. (0.033 mole) of allyl bromide with stirring over a 20-min. period. The mixture was refluxed for an additional 15 hr. with stirring. After cooling, insoluble materials were filtered off and the solvent was removed. The residue was dissolved in ether and the ethereal solution was washed with 10% sodium hydroxide solution and water. Removal of the solvent after drying afforded 2.24 g. (35%) of the desired product Ia.

C.—To a solution of 8.65 g. (0.05 mole) of 2,3-dimethyl-4-quinolinol dissolved in a sodium ethoxide solution [prepared from 1.27 g. (0.055 g.-atom) of sodium and 150 ml. of absolute ethanol] was added 6.66 g. (0.055 mole) of allyl bromide. The mixture was refluxed for 4 hr. Work-up of the reaction mixture as described above gave 6.72 g. (62%) of the desired product Ia.

TABLE II

ALLYL 2,3-DIALKYL-4-QUINOLYL ETHERS

Compd.	Yield, % Method A	Method B	Method C	B.p., °C. (mm.)	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N	Picrate[a] m.p., °C.
Ia	46	35	62	120–121 (0.15)	$C_{14}H_{15}NO$	78.84	7.09	6.59	78.93	7.16	6.45	163[b]
Ib	45	42	59	122 (0.08)	$C_{16}H_{17}NO$	80.30	7.16	5.85	80.46	7.18	5.71	133–134
Ic	47	43	67	138–139 (0.1)	$C_{17}H_{19}NO$	80.57	7.56	5.53	80.44	7.63	5.49	115.5–116

[a] All of the picrates were crystallized from ethanol and had elemental analyses in agreement with theory. [b] Lit.[10] m.p. 161°.

The other allyl ethers (Ib and Ic) were prepared from 3-allyl-2-methyl-4-quinolinol and IIa, respectively, and the results are listed in Table II.

Rearrangement of the Allyl Ethers (Ia–c).—Ia (5.0 g.) was heated without solvent at 200° for 30 min. The reaction mixture was digested with benzene and the insoluble crystals were collected by filtration to give 4.59 g. (92%) of 2-(3-butenyl)-3-methyl-4(1H)-quinolone (IIa), m.p. 260–261°. Recrystallization from ethanol afforded colorless pillars, m.p. 261–262°.

The benzene-soluble part of the reaction mixture was chromatographed on alumina and eluted with benzene–chloroform (1:1) to give two fractions. The initial fraction afforded 100 mg. (2%) of 1-allyl-2,3-dimethyl-4(1H)-quinolone (IIIa) as colorless pillars, m.p. 133–134°, on recrystallization from benzene–petroleum ether (b.p. 60–90°) (1:1). The next fraction gave 105 mg. (2.1%) of 1,4-dimethyl-2,3-dihydropyrrolo[1,2-*a*]quinolin-

TABLE III
REARRANGEMENT PRODUCTS

Starting material	Compd.	Yield,[a] %	M.p., °C.	Formula	Calcd., %			Found, %			Infrared,[b] cm.$^{-1}$			N.m.r.,[c] τ units (coupling const., J, c.p.s.)	
					C	H	N	C	H	N	C=O	NH	CH=CH$_2$	Benzene protons[d]	CH$_3$
Ia	IIa	92.0	261–262[e]	$C_{14}H_{15}NO$	78.84	7.09	6.59	78.85	7.06	6.33	1640	3272	997, 921		
	IIIa	2.0	133–134[f]					78.95	7.16	6.33	1620	...	987, 925	1.59 (1), 2.31–2.91 (3)	7.65 s, 7.88 s
	IVa	2.1 (58)	191–192[f]					78.66	7.32	6.39	1625	...	...	1.54 (1), 2.36–2.91 (3)	7.89 s, 8.51 d (J = 6.5)
Ib	IIb	90.4	243–244[e]	$C_{16}H_{17}NO$	80.30	7.16	5.85	80.49	7.17	5.79	1639	3272	991, 906		
	IIIb	3.2	98–98.5[f]					80.30	7.16	5.85	1620	...	995, 911	1.56 (1), 2.26–2.85 (3)	7.60 s
	IVb	4.1 (24)	69–70[g]					80.20	7.27	5.82	...	...	995, 916	1.89–2.76 (4)	8.43 d (J = 6.5)
Ic	IIc	90.0	239–240[e]	$C_{17}H_{19}NO$	80.57	7.56	5.53	80.63	7.61	5.57	1633	3267	994, 920		
	IIIc	2.0	83.5–84.5[g]					80.53	7.69	5.43	1620	...	994, 921	1.54 (1), 2.29–2.87 (3)	7.77 s
	IVc	0.6 (73)	200–201[h]					80.75	7.59	5.43	1622	...	993, 919	1.57 (1), 2.27–2.87 (3)	7.87 s, 8.44 d (J = 6.6)

[a] The value in parenthesis indicates yield in the cyclization method. [b] Spectra of IIa–c were determined in Nujol mull. [c] s = singlet, d = doublet. [d] The number in parenthesis indicates number of protons. [e] Recrystallized from ethanol. [f] Recrystallized from benzene–petroleum ether. [g] Recrystallized from petroleum ether. [h] Recrystallized from benzene.

5(1H)-one (IVa) as colorless needles, m.p. 191–192°, on recrystallization from benzene–petroleum ether (1:1).

The other allyl ether (Ib and Ic) were treated at 200° for 30 min. and the results are listed in Table III.

Chlorination of IIa–c with Phosphorus Oxychloride. General Procedure.—A mixture of 2–3 g. of each of the rearrangement products (IIa–c) and 10–15 ml. of phosphorus oxychloride was heated under reflux for 2 hr., and the excess phosphorus oxychloride was removed under reduced pressure. The residual sirup was poured into ice–water and made alkaline with 20% sodium hydroxide solution. The precipitate was extract with chloroform; the extract was washed with water and dried over magnesium sulfate. After removal of the solvent, compounds Va–c were obtained. The products were purified by crystallization or distillation.

The results are shown Table IV.

General Procedure for the Preparation of Alkylquinolines (VIa–c). A. Alkylation with Propyl Bromide.—A mixture of 1.57 g. (0.01 mole) of 2,3-dimethylquinoline and 0.43 g. (0.011 mole) of sodamide in 50 ml. of liquid ammonia was stirred for 1 hr. at about −50°. To the resulting solution of sodium salt of 2,3-dimethylquinoline was added 1.35 g. (0.011 mole) of propyl bromide and the mixture was refluxed (inner temperature, about −33°) for 30 min. with stirring. After evaporation of the liquid ammonia, a small amount of water was added to the residue and the precipitated oil was extracted with ether. The ethereal extract was washed with water and dried over magnesium sulfate. Removal of the solvent gave 1.82 g. of an oil, which was chromatographed on alumina and eluted with benzene. The initial fraction afforded 1.41 g. (71%) of a colorless oil (VIa), b.p. 105–106° (0.15 mm.), on distillation. The next fraction resulted in the recovery of 0.33 g. (21%) of 2,3-dimethylquinoline.

The other compounds (VIb and VIc) were prepared from VII and VIa, respectively, and the results are shown in Table IV.

B. Catalytic Hydrogenation of 4-Chloroquinolines (Va–c).—A solution of 4 mmoles of each of the 4-chloroquinolines Va–c in 20 ml. of absolute ethanol containing 4 mmoles of sodium acetate and 200 mg. of 5% palladium on carbon was hydrogenated at atmospheric pressure. After hydrogen uptake ceased, the catalysts and the solvent were removed. The residue was dissolved in ether and the ethereal solution was washed with water. Removal of the solvent after drying gave a colorless oil, which was purified by distillation. The resulting products were identical with the corresponding samples prepared by the method A (Table IV).

2-Methyl-3-propylquinoline (VII).—Chlorination of 5.0 g. of 3-allyl-2-methyl-4-quinolinol[12] with 20 ml. of phosphorus oxychloride by the usual manner afforded 5.1 g. (93.7%) of 3-allyl-4-chloro-2-methylquinoline as colorless needles, m.p. 35–35.5°, b.p. 120° (0.15 mm.).

Anal. Calcd. for $C_{13}H_{12}ClN$: C, 71.72; H, 5.52; N, 6.44. Found: C, 71.81; H, 5.63; N, 6.47.

Hydrogenation of 5.0 g. of this compound in 50 ml. of absolute ethanol over 2.0 g. of sodium acetate and 1.0 g. of 5% palladium on carbon resulted in absorption of 2.0 equiv. of hydrogen when reaction ceased. Work-up of the reaction mixture in the usual manner afforded 3.94 g. (92%) of VII as colorless pillars, m.p. 34°, b.p. 115–116° (0.1 mm.).

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.21; H, 8.19; N, 7.45.

General Procedure for the Cyclization of IIa–c.—A mixture of 500 mg. of the C-allyl compound IIa–c and 300 mg. of anhydrous zinc chloride was heated at 200–210° for 3 hr. After cooling, the reaction mixture was digested with 10% aqueous ammonia and extracted with chloroform. The extract was washed with 10% sodium hydroxide and water and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatograhy on alumina, followed by recrystallization. The resulting products were identical with the tricyclic compounds IVa–c obtained by the rearrangement reactions (Table III). The compound IVb was also prepared from IIb and pyridine hydrochloride according to the method of our previous work.[12]

Attempted Equilibration of the C-Allyl Compounds (IIa–c).—A 1.0-g. sample of each of the C-allyl compounds was heated at 200° for 30 min. without solvent. The reaction mixture was digested with benzene and the benzene-insoluble crystals were collected by filtration resulting in the recovery of over 950 mg. of the respective unaltered compounds. Chromatography of the

TABLE IV

Compd.	Yield, %	B.p., °C. (mm.)	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N	Picrate[a] m.p., °C.
Va	91	58–58.5[b]	$C_{14}H_{14}ClN$	72.57	6.09	6.04	72.44	6.12	6.09	
Vb	92	133–134 (0.15)	$C_{16}H_{16}ClN$	74.56	6.26	5.43	74.63	6.29	5.38	94.5
Vc	90	127–128 (0.15)	$C_{17}H_{18}ClN$	75.13	6.67	5.15	75.21	6.69	5.00	144–145
VIa	71,[c] 85[d]	105–106 (0.15)	$C_{14}H_{17}N$	84.37	8.60	7.03	84.49	8.68	7.01	181–182
VIb	70,[c] 90[d]	136–137 (0.2)	$C_{16}H_{21}N$	84.53	9.31	6.16	84.59	9.50	6.08	146–147
VIc	63,[c] 85[d]	126–127 (0.15)	$C_{17}H_{23}N$	84.59	9.61	5.80	84.62	9.68	5.83	150–151

[a] All of the picrates were crystallized from ethanol and had elemental analyses in agreement with theory. [b] Melting point (crystallized from dilute ethanol). [c] Yield in method A. [d] Yield in method B.

benzene-soluble portion on alumina gave a few per cent yield of the cyclization product (IVa, IVb, or IVc). The N-allyl compound (IIIa, IIIb, or IIIc) was not detected.

Attempted Equilibration of the N-Allyl Compounds (IIIa–c).—A 500-mg. sample of each of the N-allyl compounds was heated without solvent at 200° for 30 min. Chromatography of the reaction mixture on alumina resulted in the recovery of an almost quantitative amount of the unaltered compound. Column and thin layer chromatographies showed that the C-allyl compounds and the cyclization compounds were absent in the reaction mixture.

Acknowledgment.—The author is grateful to Professor E. Ochiai, Dr. K. Takeda, and Dr. H. Kano, for their encouragement.

Species in the Polymerization of Ethylenimine and N-Methylethylenimine

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Received October 19, 1964

The polymerization of ethylenimine was studied by the use of N,N-diethylethylenimmonium chloride as a model electrophilic reagent and various amines and imines as models for the nucleophiles involved. A high level of branching is indicated. N-Methylethylenimine was used as a model for the active end group. The polymerization of N-methylethylenimine in water is very rapid but stops short of completion because of a pseudo-first-order termination reaction. In aqueous ethanol polymerization is faster but termination earlier. There is a positive salt effect.

The polymerization of ethylenimine has three known kinetic main features. The rate slows markedly with increasing conversion, the polymerization goes eventually to completion, and there is a delicate balance in concentrated solution between explosive and sedate polymerization.[1] Kern and Brenneisen[2] showed that benzoylation of polyethylenimine is incomplete and deduced the presence of 20 to 30% tertiary nitrogen in the polymer. Konnecke[3] relied on Van Slyke analyses to prove branching. Barb[4] applied to ethylenimine the Flory condensation treatment which predicts the formation of dimer as a major intermediate and proposed a head-to-head reaction of dimer as a branching mechanism which would form quaternary ethylenimmonium ions. Similar ions were detected in the hydrolysis of nitrogen mustards by Golumbic, Fruton, and Bergmann.[5] Bartlett, Ross, and Swain[6] showed that diethyl-β-chloroethylamine cyclized completely before undergoing further reaction (at a concentration of 1 *N*). Methylbis-β-chloroethylamine was used by Gurin, Crandall, and Delluva[7] to rate the reactivity of various amines. Earley, *et al.*,[8] found protonated ethylenimine to be nearly twice as reactive to strong nucleophiles as protonated N-butylethylenimine but by no means so reactive as Bartlett, Ross, and Swain[6] had found N,N-diethylethylenimmonium ion to be.

The purpose of the present investigation was to simulate the kinetics of polymerization of ethylenimine and N-methylethylenimine. The intent was to confirm the degree of branching, to show the relative importance of several branching mechanisms, and to discover, if possible, a means of control of branching. Experiments with model compounds were done to obtain the desired individual rate constants.

The representation of the polymerization of ethylenimine is complicated by the probable participation of three electrophilic and five nucleophilic species. Those involved in acid-catalyzed polymerization are given below. If an alkylating agent is used to initiate polymerization, further species are added. The quaternary immonium species III would result from the attack of V on any of the electrophiles, a reaction which may be described as "head-to-head" polymerization. A branched polymer (VIII) would result either from a reaction of III or from the attack of a mid-chain nitrogen (VII) upon any of the electrophiles. The quaternary IX is that branched polymer which results from reactions of VIII. There are therefore two distinct causes of branching: the head-to-head reaction and reactions of VII and VIII.

The data to be simulated is not the over-all conversion rate which is insensitive to the individual simultaneous reactions. Rather, it is the analytically determined degree of branching and the general kinetic

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