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THE WITTIG REARRANGEMENT OF THE ALLYL ETHERS OF 2-QUINOLINE-METHANOL AND 9-FLUORENOL. ON THE SNi' MECHANISM

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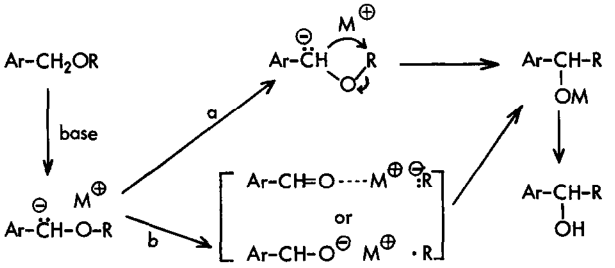
During the past twenty years, the base-catalyzed rearrangement of certain benzyl and benzhydryl ethers to alcohols (the so-called Wittig Rearrangement) (1) has been investigated by Wittig and his co-workers(2) and by several other groups (3). Although most of the earlier workers (2, 3) have supported an intramolecular displacement mechanism proceeding through a carbanion intermediate, course a in eq. 1, some recent studies have proposed an alternative cleavage-recombination mechanism, course b in eq. 1.

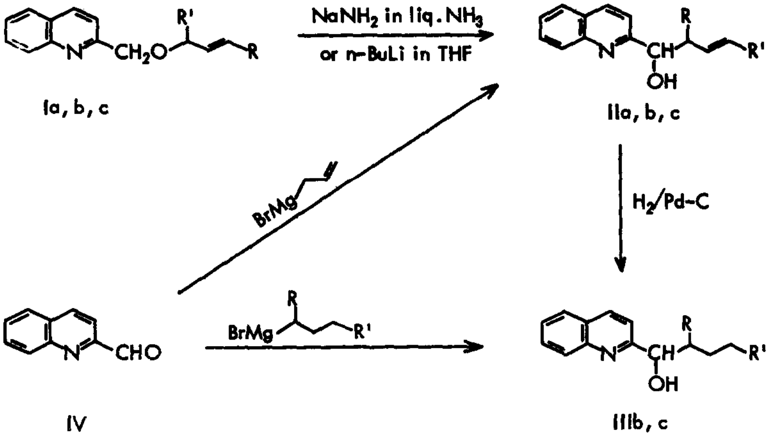


(1)

M⊕ : Metal cation of a using base

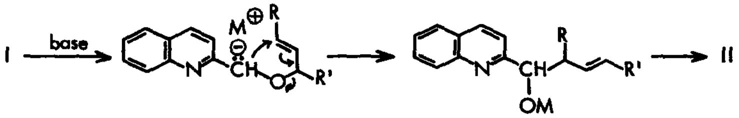
Schollkopf and his co-workers (4) observed partial racemization in the rearrangements of optically active benzyl sec-butyl ether and benzyl 1-methyl-1-phenyl propyl ether and claimed that a cleavage-recombination reaction involving initial expulsion of the migrating group as a carbanion was occurring. Lansbury and his co-workers (5) suggested that a cleavage-recombination mechanism involving free radical pairs accommodated best all of their experimental findings (5, 6). Our interest was focused on the mechanism of Wittig rearrangement of some ethers possessing an allylic group as a migrating group.

Three kinds of allyl quinaldyl ethers (I) were prepared by the reaction of 2-chloromethylquinoline with sodium allyloxide, 1-methylallyloxide, and crotyloxide in almost quantitative yields. Treatment of the allyl ether Ia, b.p$_{0.4}$ 108-109°; $\nu_{max}^{CHCl_3}$ 1648, 990, and 930 cm^{-1} (-CH=CH$_2$), with sodium amide in liquid ammonia at -33° for 2 hr. afforded a 68% yield of allyl-2-quinolylcarbinol (IIa), b.p$_{0.25}$ 124-125°; $\nu_{max}^{CHCl_3}$ 3368 (OH) and 989 and 918 (-CH=CH$_2$) cm^{-1}, identical with the sample synthesized by Grignard reaction of quinaldaldehyde (IV) with allylmagnesium bromide, and a 28% recovery of Ia. Similarly, the 1-methylallyl ether (Ib), b.p$_{0.2}$ 116°; $\nu_{max}^{CHCl_3}$ 1646, 991, and 927 cm^{-1} (-CH=CH$_2$), afforded a sole rearrangement product, crotyl-2-quinolylcarbinol (IIb), m.p. 56-57°; $\nu_{max}^{CHCl_3}$ 3390 (OH) and 1676 and 968 (-CH=CH-) cm^{-1}, in 74% yield, along with a 22% recovery of Ib. Rearrangement of the crotyl ether Ic, b.p$_{0.5}$ 137-138°; $\nu_{max}^{CHCl_3}$ 1675 and 967 cm^{-1} (-CH=CH-), also gave a sole product, 1-methylallyl-2-quinolylcarbinol (IIc), b.p$_{0.2}$ 119-120°; $\nu_{max}^{CHCl_3}$ 3385 (OH) and 1642, 998, and 919 (-CH=CH$_2$) cm^{-1}, in 78% yield, with a 14% recovery of Ic. Reduction product of IIb by catalytic hydrogenation over Pd-C was identical with n-butyl-2-quinolylcarbinol (IIIb), m.p. 75-76°, prepared by Grignard reaction of IV with n-butylmagnesium bromide. The structure of IIc was confirmed by identification of its reduction product with an authentic sample of sec-butyl-2-quinolylcarbinol (IIIc), b.p$_{0.2}$ 120-121°, which was independently prepared by Grignard reaction of IV with sec-butylmagnesium bromide.



a: R=R'=H, b: R=H, R'=CH$_3$, c: R=CH$_3$, R'=H

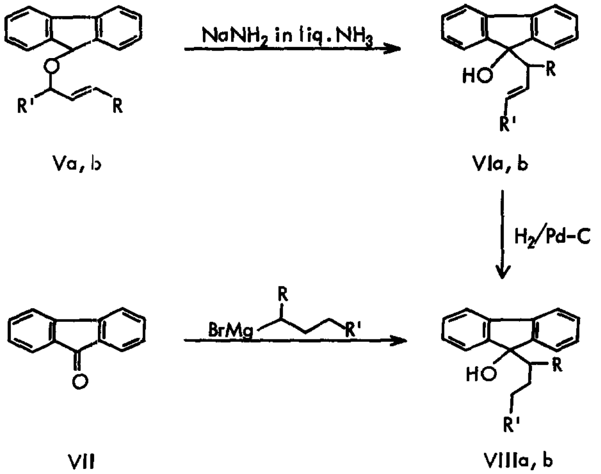
Thus, it was established that the Wittig rearrangement of allyl quinaldyl ethers induced by sodium amide in liquid ammonia, proceeds through a cyclic intramolecular process with inversion of a migrating allyl group (SNi' mechanism). The reddish coloring of the reaction mixture in the initial stage may be estimated as evidence for a carbanion intermediate.



This reaction was also examined under the conditions induced by n-butyllithium (the Schollkopf's condition). Treatment of the 1-methylallyl ether Ib with four equivalent amounts of n-butyllithium in tetrahydrofuran at -25° for 2 hr. gave a sole product, IIb, in 90% yield. Similar treatment of the crotyl ether Ic also afforded a quantitative yield of IIc. Any other rearranged products were not detected in both the reactions.

Stevens and his co-workers (7) have reported that the reaction of both of 1-methallyl 9-fluorenyl ether (Va) and crotyl 9-fluorenyl ether (Vb) with sodium n-butoxide in n-butanol at 120° affords the identical 9-crotyl-9-fluorenol (VIb) as a major product. It is difficult to interpret this result by a uniform mechanism. Then, we investigated the rearrangement of the ethers, Va and Vb, by the action of sodium amide in liquid ammonia which is more mild conditions than those used by Stevens.

Treatment of Va with sodium amide in liquid ammonia at -33° for 2 hr. afforded a sole rearranged product, VIa, m.p. 116-117°; $\nu_{max}^{CHCl_3}$ 3577 (OH) and 1670 and 974 (-CH=CH-) cm^{-1}, in 70% yield. Similarly, Vb, b.p$_{1.0}$ 151-152°; $\nu_{max}^{CHCl_3}$ 1677 and 972 cm^{-1} (-CH=CH-), rearranged to 9-(1-methylallyl)-9-fluorenol (VIb), b.p$_{0.2}$ 153-154°; $\nu_{max}^{CHCl_3}$ 3572 (OH) and 1636, 996, and 918 (-CH=CH$_2$) cm^{-1}, in 84.5% yield. Although ca. 10-20% yield of 9-fluorenone (VII) was isolated as a by-product in both of the reactions, any other rearranged products were not detected.



a: R=H, R'=CH$_3$, b: R=CH$_3$, R'=H

Catalytic hydrogenation of VIa over Pd-C gave a quantitative yield of crystals, identical with 9-n-butyl-9-fluorenol (VIIIa), m.p. 130-131°, prepared by Grignard reaction of VII with n-butylmagnesium bromide. Similarly, reduction product of VIb was also identical with 9-sec-butyl-9-fluorenol (VIIIb), b.p$_{0.5}$ 146-147°, prepared by Grignard reaction of VII with sec-butylmagnesium bromide.

Thus, it is concluded that the Wittig rearrangement, in which an allylic group migrates, proceeds through a cyclic intramolecular process with inversion of the migrating group, in contrast to that an alkyl or aralkyl group migrates by a cleavage-recombination mechanism (4, 5, 6).

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