The Structure and a Novel Type Rearrangement of a Ketol Produced by the Robinson Annelation Reaction

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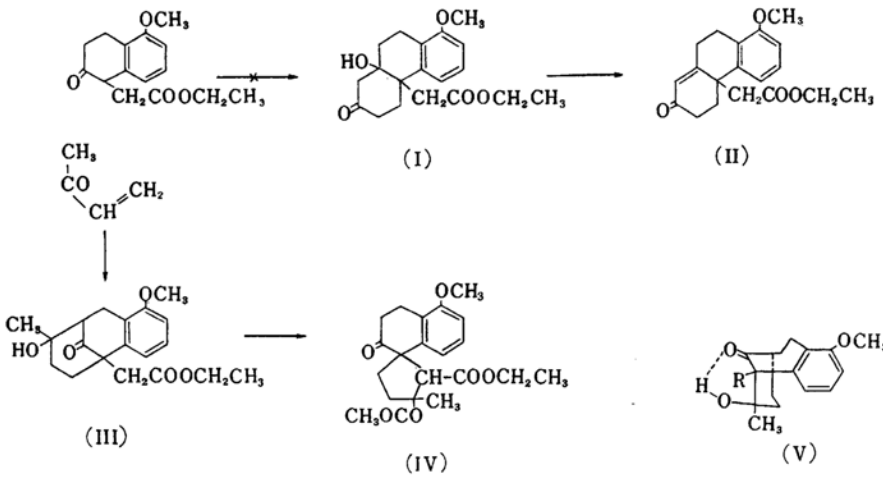
In the course of a study directed to the synthesis of a certain diterpenoid skeleton[1], the authors condensed ethyl 1, 2, 3, 4-tetrahydro-2-oxo-5-methoxy-1-naphthyl acetate[2] with methyl vinyl ketone, expecting the formation of either ketol I or its dehydration product II. However, the obtained ketol [m. p. 134~135°C; ν_{max}^{Nujol} 3380 (OH), 1733 and 1185 (ester), and 1700 cm^{-1} (ketone); λ_{max}^{MeOH} 271 (ε 1410) and 278 mμ (ε 1310); Found: C, 68.44; H, 7.10. Calcd. for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28%] was actually a bridged ring compound III. Moreover, attempted acetylation of III with isopropenyl acetate in the presence of *p*-toluenesulfonic acid resulted in a remarkable change in the carbon skeleton of compound III, a spirocyclic acetate IV [m. p. 97.5~98.5°C; ν_{max}^{Nujol} 1730 (ester) and 1715 cm^{-1} (ketone); Found: C, 67.10; H, 6.94. Calcd. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00%] being produced. The formation of a similar bridged ring ketol system through the Robinson annelation reaction was first disclosed only quite recently by W. S. Johnson and his co-workers[3]. Conversion of the skeletons III to IV seems, so far as the authors are aware, to have never been described in the literature.

The structures of both compounds III and IV were determined by the NMR spectra[4]. The spectrum of ketol III showed one sharp maximum at high applied magnetic field characteristic of proton resonance for the $-\overset{|}{\underset{|}{C}}-CH_3$ group (203 c. p. s., standard, benzene; observed relative peak area, 3.4) and is completely accounted for in terms of structure III. Further, presence of an intramolecular hydrogen bond, as indicated by the infrared spectrum (ν_{max} 3430 cm^{-1}, in 0.0046 M solution in tetrachloroethylene) clearly defines the conformation of the ketol as V. In the NMR spectrum of acetate IV, presence of a $-\overset{|}{\underset{|}{C}}-CH_3$ group and

1) T. Matsumoto and A. Suzuki, This Bulletin, 32, 1283 (1959); 33, 33 (1960).
2) T. Matsumoto and A. Suzuki, to be published.
3) W. S. Johnson, J. J. Korst, R. A. Clement and J. Dutta, *J. Am. Chem. Soc.*, 82, 614 (1960).
4) Taken on a Varian 40 MC instrument in $CDCl_3$ solution.



absence of the $-\overset{|}{\underset{|}{C}}-CH_2-CO_2-$ group are indicated respectively by the appearance of a sharp peak at 190 c. p. s. (relative peak area, 3.1) and by the disappearance of the singlet peak at 151 c. p. s. (relative peak area, 1.7) of III. The only one structure consistent with the observed findings is expressed by formula IV. The resonance line due to $-\overset{|}{\underset{|}{C}}-CH_3$ group of the acetate is shifted to the lower magnetic field by 13 c. p. s. as compared with that of the ketol. This shift might be an indication of the *cis* location of the methyl and ethoxycarbonyl groups.

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