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Chemistry

The unusual Favorskii–Nazarov reaction of dicyclopropyl ketone

(cyclopropyl bond cleavage/dianion intermediate/neutral ketone)

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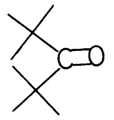
ABSTRACT Dicyclopropyl ketone under Favorskii-Nazarov reaction conditions neither gave tetracyclopropylethylene glycol nor 1,1,4,4-tetracyclopropyl-1,4-butanediol by ether incorporation as expected. The hitherto unknown 1,1,5-tricyclopropyl-1-hydroxypentan-5-one is obtained, presumably through the intermediacy of a dianion which nucleophilically attacks the neutral ketone through the cleavage of the cyclopropyl bond.

Favorskii and Nazarov (1, 2) reported that sodium reduction of di-*t*-butyl ketone (**1**) in diethyl ether yielded tetra-*t*-butylethylene glycol (**2**) and the reaction was generalized to other aliphatic ketones (3–5). Later it was shown by Eberson (6) that the product from Favorskii-Nazarov reaction of (**1**) was 1,1,4,4,-tetra-*t*-butyl-1,4-butanediol (**3**). The dianion formation mechanism suggested by Eberson for ether incorporation was also substantiated by the work of Bartlett *et al.* (7).



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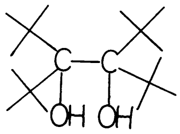

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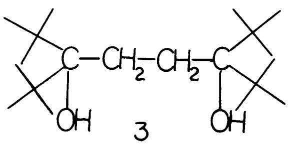

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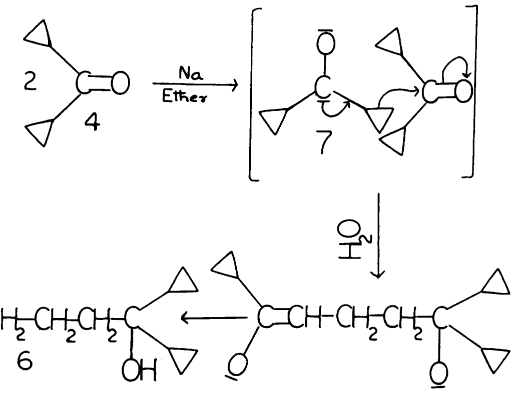
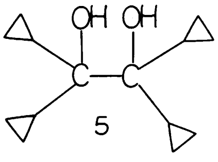
We now wish to report the unusual behavior of dicyclopropyl ketone (**4**) under Favorskii–Nazarov conditions. This gave, in addition to the reduction product dicyclopropyl carbinol, a 30% yield of the unexpected and hitherto unknown 1,1,5-tricyclopropyl-1-hydroxypentan-5-one (**6**), with a boiling point at 0.3 torr (1.33×10^2 Pa) = 124°; the analysis (%) was calculated for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. We found: C, 75.42; H, 9.97. The mass spectrum showed peaks at mass/electron: 222 (0.08%, M^+), 204 (13.5%, M^+ —H_2O), 120 (18.3%, M^+ —H_2O—$CprCOCH_3$), 108 (12.4%), 69 (69.6%, $CprCO^+$), 55 (14.7%, $CprCH_2^+$), 41 (32.5%, Cpr^+), 40 (100%, $C_3H_4^+$), 18 (72%). Infrared analysis (liquid film, cm^{-1}): 3480 (medium, OH), 3100 (sharp, CprCH), 3000–2900 (medium, aliphatic CH), 1690 (sharp, CO). Proton magnetic resonance spectroscopy was performed at 60 MHz, $CDCl_3$, and 37°. The following δ values were obtained: 3.3 (t, unsymmetrical, 2H), 2.3 (medium, 6H, includes OH), 1.3 (medium, 6H), 0.7 (medium, 8H). The carbon-13 nuclear magnetic resonance spectroscopy (100 MHz, and $CDCl_3$, in ppm from external tetramethyl silane, and proton noise decoupled) assignments were confirmed by off-resonance experiment: 212.58 (CO), 71.15 (—COH—), 45.13 (—CH_2CO—), 43.35 (—CH_2COCpr), 21.52 (methine of CprCO—), 19.78 (methine of Cpr_2COH—), 19.67 ($CH_2CH_2CH_2$), 11.72 (methylene of CprCO—), 1.05, 1.82 (methylene of Cpr_2COH—). The expected tetracyclopropylethylene glycol (**5**) was not obtained (8).*





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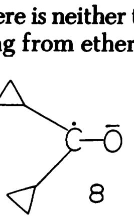
The formation of (**6**) can be rationalized by the following mechanism involving the intermediacy of the dianion (**7**). The negative charge on the carbon of the (**7**) is delocalized into the cyclopropyl ring, and thus a nucleophilic attack of the dianion through the cleavage of the cyclopropyl bond on the neutral ketone (**4**) results in the product (**6**).

The general mechanism for glycol formation in the Favorskii-Nazarov reaction is assumed to involve a radical anion (1–5). The intermediacy of radical anion (**8**) in the present studied reaction can be ruled out as glycol (**5**) is not formed. Thus, the reaction of dicyclopropyl ketone with sodium in ether is apparently quite different from that of other aliphatic ketones or di-*t*-butyl ketone as there is neither the formation of 1,2-diol (**5**), nor 1,4-diol (**9**) arising from ether incorporation.



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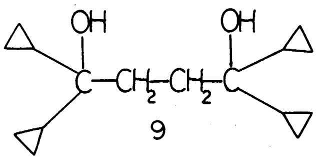
Abbreviation: Cpr, cyclopropyl.

* The diol (**5**) was obtained as a product from McMurry olefin synthesis reaction (ref. 8) of dicyclopropyl ketone.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