# KETONES OF THE BICYCLO[2.2.1]HEPTANE SERIES IN THE SYNTHESIS OF GEMINAL DIAMIDES

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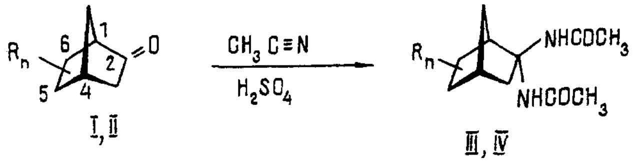
The transformations of isofenchone and of 5-exo-ethylnorcamphor under the conditions of the Ritter reaction have been studied. These ketones undergo transformations similar to those that have been described for their structural analogues camphor and isocamphanone, as a result of which the corresponding geminal diamides are formed. The structures of the compounds synthesized were shown by IR, mass, and $^1H$ NMR spectroscopies.

In the course of the present investigation we have studied the transformations under the conditions of the Ritter reaction of isofenchone (1,5,5-trimethylbicyclo[2.2.1]heptan-2-one) (I) and of 5-exo-ethylnorcamphor (5-exo-ethylbicyclo[2.2.1]heptan-2-one) (II). It has been established that under these conditions ketones (I) and (II) undergo transformations analogous to those that have been described for camphor and isocamphanone [1, 2], leading to N,N'-diacetyl-2,2-diamino-1,5,5-trimethylbicyclo[2.2.1]heptane (III) and N,N'-diacetyl-2,2-diamino-5-exo-ethylbicyclo[2.2.1]heptane (IV), respectively. The structures of compounds (III) and (IV) have been shown on the basis of the results of IR, mass, and $^1H$ NMR spectroscopies.



$R_n = 1,5,5\text{-}(CH_3)_3$ (I, III); 5-exo-$C_2H_5$ (II, IV)

Thus, it may be concluded that the capacity for interacting with nitriles under the conditions of the Ritter reaction to form the corresponding geminal diamides is a common property of ketones of the bicyclo[2.2.1]heptane series, while all the ketones studied reacted without any rearrangement of the initial hydrocarbon skeleton.

## EXPERIMENTAL

The initial isofenchone (I) was obtained by the potassium dichromate oxidation of isofenchol [3], and had bp 92°C (4 mm Hg), $n_D^{20}$ 1.4624. According to the literature [4]: bp 201°C, $n_D^{20}$ 1.4619.

5-exo-Ethylnorcamphor (II) (technical product) was purified by rectification and had bp 78°C (4 mm Hg), $n_D^{20}$ 1.4718. According to the literature [5]: bp 90°C (12 mm Hg), $n_D^{20}$ 1.4711.

The Ritter reaction was conducted by the standard procedure [1, 2].

N,N'-Diacetyl-2,2-diamino-1,5,5-trimethylbicyclo[2.2.1]heptane (III) was obtained from 2.5 g of the ketone (I), 5 ml of acetonitrile, and 5.2 ml of conc. $H_2SO_4$ with a yield of 1.8 g (43%). mp 248°C (ethanol). IR spectrum ($\lambda_{max}^{KBr}$, $cm^{-1}$): 3400, 3300 (N–H), 2980, 2880 (C–H), 1660 (C=O, amide I), 1550 (NH). Mass spectrum (m/z): 252 ($M^+$, 11%), 211, 196, 178, 166, 152, 136, 121, 110, 99, 95, 80, 59, 57, 43 (100%), 41. PMR spectrum (δ, ppm, $CDCl_3$), 0.97 (s, 3H, 5-$CH_3$-exo), 0.98 (s, 3H, 5-$CH_3$-endo), 1.06 (s, 3H, 1-$CH_3$), 1.24 (d, 1H, $^2J$ =

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12.8 Hz, 6-H-exo), 1.58 (d, 1H, $^2J$ = 9.6 Hz, 7-H-anti), 1.65 (d, 1H, $^3J$ = 4.5 Hz, 4-H), 1.82 (d, 1H, $^2J$ = 9.6 Hz, 7-H-syn), 1.91 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.07 (dd, 1H, $^2J$ = 15.6 Hz, $^3J$ = 4.5 Hz, 3-H-exo), 2.37 (d, 1H, $^2J$ = 15.6 Hz, 3-H-endo), 6.14 (1H, NH), 6.30 (1H, NH).

N,N'-Diacetyl-2,2-diamino-5-exo-ethylbicyclo[2.2.1]heptane (IV) was obtained from 2.2 g of the ketone (II), 5 ml of acetonitrile, and 5.2 ml of conc. $H_2SO_4$ with a yield of 1.6 g (42%). mp 207°C. IR spectrum $\lambda_{max}^{KBr}$, $cm^{-1}$): 3400, 3310 (N–H), 2960, 2870 (C–H), 1660 (C=O, amide I), 1550 (NH). Mass spectrum (m/z): 238 ($M^+$, 30%), 195, 181, 179, 167, 152, 138, 122, 109, 94, 86, 63, 43 (100%). PMR spectrum (δ, ppm, $CD_3OD$): 0.96 (m, 5H, 5-$C_2H_5$), 1.19 (m, 1H, 5-H-endo), 1.31 (dd, 1H, $^2J$ = 13.2 Hz, $^3J_{endo-endo}$ = 9.6 Hz, 6-H-endo), 1.40 (d, 1H, $^2J$ = 10.8 Hz, 7-H-anti), 1.53 (dd, 1H, $^2J$ = 13.2 Hz, $^3J_{endo-exo}$ = 3.6 Hz, 6-H-exo), 1.56 (m, 1H, 4-H), 1.58 (d, 1H, $^2J$ = 10.8 Hz, 7-H-syn), 1.87 (s, 3H, $COCH_3$), 1.90 (s, 3H, $COCH_3$), 1.92 (d, $^2J$ = 18.0 Hz, 3-H-endo), 2.16 (dd, 1H, $^2J$ = 18.0 Hz, $^3J$ = 4.8 Hz, 3-H-exo), 2.82 (br.s, 1H, 1-H).

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# RETRO-MICHAEL REACTION OF 28-METHOXY-18,19-SECOLUPANE-18,19-DIONE DERIVATIVES

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The interactions with KOH in boiling diethyleneglycol of 3β,28-dimethoxy- and 3β-acetoxy-28-methoxy-18,19-secolupane-18,19-diones have been studied. In the first case, 3β-methoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one and the corresponding 18-ol were isolated from the mixture of products, and in the second case 3β-hydroxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one — which was also obtained by an analogous reaction from 3β-acetoxy-18,19-secolupan-18,19-dione — and 3β-hydroxy-19,20,21,22,28,29,30-heptanor-18,19-secolupan-18-one. Thus, it has been found that in this case the retro-Michael reaction is accompanied by 28-demethoxylation and partially by 28-demethoxymethylation.

The retro-Michael reaction of triterpene 1,5-diones, which takes place when they are boiled with KOH in diethyleneglycol, has been used in structural investigations and, in particular, in the refinement of the structures of 3-acetoxy-13,17-secodammarane-13,17-dione [1] and of 6-acetoxy-17,21-secozeorinane-17,21-dione [2]. Then, taking 4,5-secolupan-3,5-dione as an example, it was found that an analogous cleavage took place on vacuum distillation with an alkaline glass fractionating column and that under these conditions the yield of de-A-(10βH)lupan-5-one was almost twice as great as the yield of the de-A-(10βH)lupan-5-ol formed on reaction with KOH in diethyleneglycol [3]. In 1986 it was found that the retro-

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