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## Abstract

## Full Text

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# SYNTHESIS OF 1-METHYL-1,2-DICYCLOPROPYLCYCLOPROP

Many hydrocarbons with one cyclopropyl group have been described in the literature, only five hydrocarbons with two cyclopropyl groups ([1]), and not a single hydrocarbon with three or more cyclopropyl groups in the molecule is mentioned. This is explained by the difficulties of synthesizing such compounds by known routes, for example 1-methyl-1,2-dicyclopropylcyclopropane. The most thoroughly studied route for the synthesis of cyclopropane hydrocarbons according to the scheme: $\alpha,\beta$-unsaturated ketone $\rightarrow$ pyrazoline $\rightarrow$ hydrocarbon—in the present case proved unsuitable for the synthesis of a hydrocarbon with three adjacent cyclopropyl groups because of the difficulty of obtaining and the low stability of the corresponding starting unsaturated ketone—1,3-dicyclopropylbuten-2-one-1 ([2]).

In this connection we chose another route for the synthesis of this cyclopropane hydrocarbon according to the scheme:

$$2\,\begin{matrix}H_2C\\H_2C\end{matrix}\!\!\rangle CH{-}C(=O)CH_3 + NH_2NH_2 \longrightarrow \begin{matrix}H_2C\\H_2C\end{matrix}\!\!\rangle CHC(CH_3)=N{-}N=C(CH_3){-}CH\begin{matrix}CH_2\\CH_2\end{matrix}\!\!\rangle \xrightarrow[100^\circ C]{(COOH)_2}$$

$$\longrightarrow \begin{matrix}H_2C\\H_2C\end{matrix}\!\!\rangle CH{-}C(CH_3)\;\begin{matrix}CH_2\\NH{-}N\end{matrix}\!\!\rangle C{-}CH\langle\begin{matrix}CH_2\\CH_2\end{matrix} \xrightarrow[230^\circ C]{KOH} \begin{matrix}H_2C\\H_2C\end{matrix}\!\!\rangle CH{-}C(CH_3)\;CH_2{-}CH-CH\langle\begin{matrix}CH_2\\CH_2\end{matrix}$$

The starting methyl cyclopropyl ketone was prepared by the method described by us ([3]); increasing the scale of the experiment did not cause a decrease in the yield of methyl cyclopropyl ketone. Starting from methyl cyclopropyl ketone, we for the first time synthesized the corresponding ketazine in 93% yield. The ketazine of methyl cyclopropyl ketone is practically unchanged on heating to boiling with KOH, $CHCl_3$, and $KHSO_4$. It could be assumed that the use of oxalic acid as a catalyst for the isomerization of the ketazine of methyl cyclopropyl ketone might cause opening of the cyclopropyl ring, as occurs under the action of acids on cyclopropane carbinols ([4]).

However, as it turned out, isomerization of the ketazine of methyl cyclopropyl ketone to pyrazoline under the action of an equimolecular amount of oxalic acid at 100° proceeds without opening of the trimethylene ring, which is confirmed

by the absence, in the Raman spectrum of the hydrocarbon obtained, of the characteristic frequency in the region 1600–1640 $cm^{-1}$. In the case of a deficiency of oxalic acid, the corresponding portion of the ketazine is recovered unchanged from the reaction. On standing for two days without heating in contact with oxalic acid and subsequent treatment with alkali solution, the ketazine almost completely decomposes to the original methyl cyclopropyl ketone. Addition of methyl cyclopropyl ketone at the beginning of the reaction does not reduce the decomposition of the ketazine, but improves the conditions for mixing the ketazine with the acid.

With increasing time of heating the mixture of ketazine with acid, formation of polymeric products increases. On the other hand, decreasing it leads to a lower yield of pyrazoline.

For each ketazine there apparently exists its own optimum heating time for isomerization. For methylcyclopropyl ketone ketazine it is 1.5–2 h. With good stirring there is no need for an excess of oxalic acid. The synthesis conditions we selected made it possible to obtain 1-methyl-1,2-dicyclopropylcyclopropane in 52% yield. Consideration of the features of the Raman spectrum of this hydrocarbon makes it possible to conclude that cis- and trans-forms are present.

## Experimental Part

**Acetopropyl chloride** was obtained from 1111 g of acetopropyl alcohol and 2200 ml of hydrochloric acid saturated with hydrogen chloride (from 1350 ml of HCl and 1050 ml of $H_2SO_4$), in an amount of 994 g, with a yield of 76% ([3]).

**Methylcyclopropyl ketone** was obtained from 2040 g of acetopropyl chloride and 1880 g of granular chemically pure KOH, in an amount of 1337 g, with a yield of 93.8% ([3]).

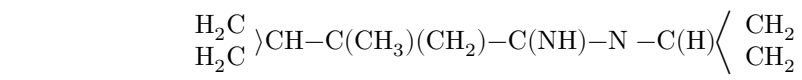
**Ketazine of methylcyclopropyl ketone**

$$\begin{matrix} H_2C \\ H_2C \end{matrix} \rangle CHC(CH_3) = N{-}N = C(CH_3)CH\langle \begin{matrix} CH_2 \\ CH_2 \end{matrix}$$

To 420 g of methylcyclopropyl ketone, with stirring, 125 g of hydrazine hydrate in 135 ml of ethyl alcohol was added. The mixture was then heated with stirring for 10 h on a boiling water bath. The upper layer, together with the ether extracts from the lower layer, was dried with caustic potash. After distillation, 6.3 g of methylcyclopropyl ketone, 16.5 g of the alkylidenehydrazine of methylcyclopropyl ketone, and 381 g (93%) of methylcyclopropyl ketone ketazine were isolated, b.p. 137° (44 mm); $n_D^{20}$ 1.5140; $d_4^{20}$ 0.9456; $MR$ found 52.29; calculated 52.58.

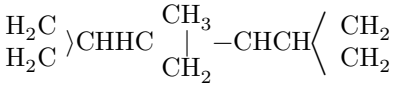
| | | | | |
|---|---|---|---|---|
| | Found, %: | C 73.06; 73.19; | H 9.83; 9.87 |
| $C_{10}H_{16}N_2$. | Calculated, %: | C 73.12; | H 9.81 |

**5-Methyl-3,5-dicyclopropylpyrazoline**



To 45 g of dry oxalic acid, with stirring, a mixture of 82 g of methylcyclopropyl ketone ketazine and 42 g of methylcyclopropyl ketone was added. The contents of the flask were heated with stirring for 1.5 h on a boiling water bath and then cooled with ice water. After this, a solution of alkali (100 g of KOH in 150 ml of water) was added to the flask, and the contents of the flask were extracted 5 times with ether. The ether extracts (750 ml) were dried with caustic potash. After removal of the ether, 66 g of methylcyclopropyl ketone and 38 g (46.3%) of pyrazoline were isolated, b.p. 136° (37 mm); $n_D^{20}$ 1.5120; $d_4^{20}$ 0.9603; $MR$ found 51.32; calculated 51.77. Elemental analysis of the compound was not carried out, since even at room temperature evolution of nitrogen from it was noticeable.

**1-Methyl-1,2-dicyclopropylcyclopropane**



125 g of 5-methyl-3,5-dicyclopropylpyrazoline was slowly distilled to 230° over 9 g of granular caustic potash in a glass flask. The caustic potash was added as necessary in portions of 3 g. After drying with caustic potash, the product was distilled in vacuum. The hydrocarbon fraction was

washed three times with 50% acetic acid (20 ml portions), neutralized with soda, and dried over caustic potash. After fivefold distillation under vacuum, 25 g was obtained (52%, calculated on the pyrazoline introduced into the reaction) of 1-methyl-1,2-dicyclopropylcyclopropane, b.p. 80° (49 mm); 158° (753 mm); $n_D^{20}$ 1.4574; $d_4^{20}$ 0.8504; $MR$ found 43.66; calculated 44.11 (5).

Found, %: C 88.19; 88.12; H 11.68; 11.69
$C_{10}H_{16}$. Calculated, %: C 88.16; H 11.84

**Combination light-scattering spectrum of 1-methyl-1,2-dicyclopropylcyclopropane***

$\Delta\nu$, $cm^{-1}$: 262 (1); 319 (5sh); 374 (1); 425 (2sh); 464 (1); 521 (0); 555 (0); 588 (0); 641 (5sh); 657 (2sh); 743 (5sh); 783 (1); 822 (5sh); 888 (4sh); 890 (5sh); 911 (8sh); 952 (4); 968 (1sh); 1020 (1sh); 1047 (2sh); 1113 (2sh); 1152 (1); 1175 (3sh); 1196 (10); 1212 (8); 1242 (1); 1289 (2sh); 1326 (1); 1384 (3sh); 1405 (4sh); 1432 (4); 1458 (5); 1487 (6); 2870 (1); 2914 (0sh); 3000 (10); 3052 (5).

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* The spectrum was recorded by Yu. P. Egorov, to whom the authors express their gratitude.

*Note: Figure translations are in progress. See original paper for figures.*