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Abstract

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SYNTHESIS OF SOME COMPOUNDS WITH TWO ADJACENT THREE-MEMBERED RINGS

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Among compounds whose molecule contains two three-membered rings, the literature reports: one dicarboxylic acid and its ester ([1]), two saturated aliphatic ketones ([2],[3]), one unsaturated ketone ([4],[5]), and two nitro ketones ([6],[7]), nine alcohols, and eight hydrocarbons. Such a small number of these compounds is due to the absence of simple and reliable methods for their synthesis, which makes this area of organic chemistry little studied, despite the distinctive chemical and physical properties of its representatives. Starting from isopropenylcyclopropane, we have carried out the synthesis of five compounds containing two three-membered rings per molecule. In the reaction of diazoacetic ester with isopropenylcyclopropane, the ethyl ester of the corresponding acid was obtained in a yield of ~60%, which indicates a higher reactivity of the double bond of isopropenylcyclopropane in comparison with the reactivity of the double bond of alkenes ([8]).

Dimethyl-(2-methyl-2-cyclopropyl)-cyclopropylcarbinol was obtained by us only in the reaction of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid with methyllithium.

In the interaction of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid with CH_3MgCl, a mixture of alcohols was obtained. Judging from the infrared spectrum, this mixture was dominated by the isomerization products of dimethyl-(2-methyl-2-cyclopropyl)-cyclopropylcarbinol—unsaturated alcohols (characteristic double-bond frequency 1652 (10) cm^{-1}).

We first encountered a similar instance of isomerization of a three-membered ring in the preparation of alcohols by the Grignard reaction during the synthesis of a tertiary alcohol by the action of CH_3MgBr on the ethyl ester of 2,2,3,3-tetramethylcyclopropanecarboxylic acid ([9]). Replacement of CH_3MgBr by CH_3MgCl allowed us in that case to obtain an alcohol containing no admixture of unsaturated alcohols. Evidently, dimethyl-(2-methyl-2-cyclopropyl)-cyclopropylcarbinol, having an even more complex molecule, is readily isomerized even in a weakly acidic medium at 35°.

Infrared spectra* were recorded for the compounds obtained; from these it may be concluded that, in all the remaining cases, admixtures of compounds with a double bond are absent.

Experimental Part

Isopropenylcyclopropane. Obtained by dehydration of dimethylcyclopropylcarbinol in the presence of 0.01 wt.% 100% H_2SO_4; b.p. of the hydrocarbon 70° at 759 mm, n_D^{20} 1.4257; D_4^{20} 0.7509 (literature data ([10]): b.p. 70.5° at 760 mm, n_D^{20} 1.4255; D_4^{20} 0.7513).

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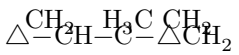
* The spectra were recorded by G. K. Gaivoronskaya, a member of the optical group of the hydrocarbon chemistry laboratory.

1-Methyl-1-cyclopropylcyclopropane

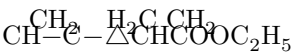


53.6 g of methylene iodide and 0.15 g of iodine were added to 16.3 g of Zn/Cu in 165 ml of abs. ether. The mixture was heated for 30 min, after which 33 g of isopropenylcyclopropane was added dropwise over 1 hour and heating was continued for 25 h. The mixture was then treated with 5% aqueous HCl, saturated potassium carbonate solution, dried, and distilled. This gave 7 g (37% based on the methylene iodide taken into the reaction) of 1-methyl-1-cyclopropylcyclopropane, b.p. 88–92° at 758 mm, which after distillation over metallic sodium had b.p. 88–89.5° at 762 mm, D_4^{20} 0.7826; n_D^{20} 1.4221; found MR_D 31.23; calculated 31.64.

Found, %:	C 87.60; 87.63, H 12.71; 12.42
C_7H_{12}. Calculated, %:	C 87.42; H 12.57

IR spectrum, cm^{-1}: 263(2), 325(2), 365(0), 395(0), 423(1), 455(1), 481(2), 586(0), 639(5), 745(0), 774(1), 818(0), 831(3), 853(3), 898(1), 933(3), 948(3), 971(0), 1071(0), 1030(1), 1044(0), 1070(1), 1103(1), 1114(1), 1165(0), 1195(8), 1235(1), 1257(1), 1298(0), 1319(2 sh), 1382(1 sh), 1427(1 sh), 1458(1 sh), 2873(2), 2900(0), 2925(2), 2940(2 sh), 3002(10 sh), 3075(3 sh).

Ethyl 2-methyl-2-cyclopropylcyclopropanecarboxylate



To 200 g of isopropenylcyclopropane and 4 g of $CuSO_4$, placed in a flask fitted with a reflux condenser, dropping funnel, and stirrer, a solution of 38.8 g of ethyl diazoacetate in 32 g of isopropenylcyclopropane was added dropwise at

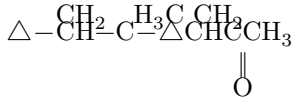
the boil. After the addition, the mixture was heated for a further 30 min, cooled, filtered from $CuSO_4$, and the excess hydrocarbon was distilled off. The resulting residue was distilled in vacuo from a Claisen flask, and then on a rectification column with an efficiency of 18 theoretical plates. This gave 34 g (59.6% based on the ethyl diazoacetate taken into the reaction) of ethyl 2-methyl-2-cyclopropylcyclopropanecarboxylate, b.p. 83° at 11 mm, D_4^{20} 0.9613; n_D^{20} 1.4513; found MR_D 47.14; calculated 47.34.

Found, %:	C 71.20; 71.40; H 9.65; 9.72
$C_{10}H_{16}O_2$. Calculated, %:	C 71.39; H 9.58

IR spectrum, cm^{-1}: 265(0 sh), 316(1 sh), 355(2 sh), 390(1), 423(1), 476(1 sh), 523(1 sh), 586(1), 618(1), 638(8), 760(7 sh), 775(1 sh), 818(5 sh), 832(4 sh), 845(6), 859(5), 898(3), 932(3), 945(4 sh), 962(3 sh), 1013(2 sh), 1045(3 sh), 1072(1), 1096(2 sh), 1115(3 sh), 1171(2 sh), 1195(10), 1244(3 sh), 1300(4 sh), 1355(1), 1384(5), 1405(5), 1428(3), 1448(5 sh), 1468(6 sh), 1724(6), 2960(1 sh), 3005(10 sh), 3075(5 sh).

2-Methyl-2-cyclopropylcyclopropanecarboxylic acid. Obtained by saponification of ethyl 2-methyl-2-cyclopropylcyclopropanecarboxylate by heating with 20% aqueous-alcoholic KOH solution for 15 h; b.p. 120° at 11 mm, D_4^{20} 1.0328; n_D^{20} 1.4710; found MR_D 37.93; calculated 37.92.

Methyl(2-methyl-2-cyclopropyl)cyclopropyl ketone



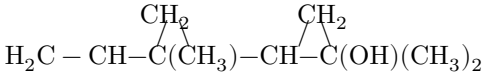
From 4.5 g of metallic lithium and CH_3Cl in 200 ml of abs. ether, CH_3Li was obtained; to this, at 35°, a solution of 14 g of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid in an equal volume of ether was added. The mixture was heated for 9 h on a water bath and decomposed with water. The ethereal solution was dried over solid KOH and distilled. 4 g of methyl-(2-methyl-2-cyclopropyl)-cyclopropyl ketone was obtained, yield 29%, b.p. 76–77° at 12 mm, D_4^{20} 0.9047; n_D^{20} 1.4588; found MR_D 41.74; calculated 41.07.

Found, %:	C 77.68; 77.90; H 10.78; 10.51
$C_9H_{14}O$. Calculated, %:	C 78.21; H 10.21

Raman spectrum, in cm^{-1}: 297(1sh), 390(1sh), 450(0sh), 498(0sh), 610(2), 624(4), 674(6), 686(4), 778(0), 835(6), 870(0), 931(4), 965–975(2sh, doublet), 1044(1sh), 1130(4sh), 1186–1202(2sh, doublet), 1355(1sh), 1403(2sh), 1422(2sh),

1467(3sh), 1700(6), 2880(2sh), 2896(1sh), 2928(6), 2954(3sh), 2970(3sh), 3010-3025(2sh, doublet).

Dimethyl-(2-methyl-2-cyclopropyl)-cyclopropylcarbinol



A. To CH_3MgCl, prepared in 200 ml of abs. ether from 10 g of Mg, 21 g of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid was added. The mixture was heated for 8-10 h on a water bath and decomposed only with water. The organic layer was dried over K_2CO_3 and distilled on a vacuum fractionating column. A mixture of alcohols was obtained with b.p. 86° at 25 mm, D_4^{20} 0.8850; n_D^{20} 1.4657; found MR_D 48.24; calculated 47.11.

Found, %:	C 78.06; 77.96; H 11.50; 11.70
$C_{10}H_{18}O$. Calculated, %:	C 77.86; H 11.76

Raman spectrum, in cm^{-1}: 635(2sh), 650(3), 710(5sh), 717(5sh), 763(1), 790(1), 813(1), 845(5sh), 903(5sh), 933(1), 970(2sh), 1002(1), 1013(3sh), 1041(2), 1102(1), 1172(3sh), 1198(5), 1230(5), 1300(2), 1325(1), 1380(4sh), 1398(2sh), 1443(3sh), 1463(4sh), 1600(3sh), 1652(10), 287(3sh), 2915(1sh), 2935(2sh), 2973(1sh), 2997(3sh), 3014(5sh), 3080(10).

Thus, from the spectral-analysis data it is evident that isomerization of the three-membered ring occurred and a mixture of unsaturated alcohols was formed.

B. From 4.5 g of metallic lithium and CH_3Cl in 200 ml of abs. ether, $LiCH_3$ was obtained; to it, at 35°, 17 g of the ethyl ester of 2-methyl-2-cyclopropylcyclopropanecarboxylic acid was added. The mixture was heated for 8 h on a water bath, decomposed with water, and the aqueous layer was extracted with ether. The ethereal solution was dried over $CaCl_2$ and distilled. An alcohol was obtained with b.p. 88.5-89° at 22 mm, weight 11 g, yield 70%, D_4^{20} 0.9037; n_D^{20} 1.4595; found MR_D 46.70; calculated 47.11.

Found, %:	C 77.36; 77.39; H 11.57; 11.80
$C_{10}H_{18}O$. Calculated, %:	C 77.86; H 11.76

Raman spectrum, in cm^{-1}: 258(0), 293(1sh), 390(0), 408(0), 465(0), 630(0), 652(1), 668(1sh), 712(2sh), 783(1sh), 822(1sh), 832(1sh), 845(2), 863(1), 880(0), 903(1sh), 934(1), 948(1), 968(1), 1069(0), 1093(0), 1130(0), 1177(1sh), 1195(5),

1250(0), 1298(1 sh), 1400(1 sh), 1422(1), 1452(2 sh), 1460(2 sh), 2865(2 sh), 2910(3 sh), 2932(3 sh), 2968(3 sh), 3000(10), 3065(3 sh).

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