REACTIONS OF DIAZOACETIC ESTER WITH BRANCHED ALKENES

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UDC 542.91

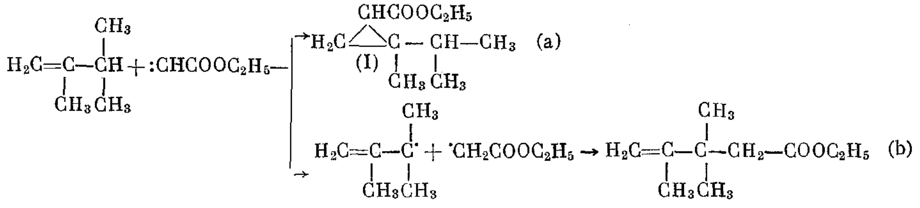
In continuation of our study of the reactions of diazoacetic ester with alkenes of various structures [1, 2] we have conducted reactions of diazoacetic ester with such branched alkenes as 2,3,3-trimethyl-1-butene, 4-propyl-3-heptene, and 3-isopropyl-2,4-dimethyl-2-pentene. These olefins were prepared by the dehydration of the corresponding alcohols in presence of iodine. It was shown by Raman spectra that only in the case of the dehydration of 3-isopropyl-2,4-dimethyl-3-pentanol did the isomerization of the alkene formed occur (presence of two characteristic C=C frequencies in the spectrum). In further work, therefore, 3-isopropyl-2,4-dimethyl-3-pentanol was dehydrated by Chugaev's method [3], which excludes or considerably diminishes the isomerization of the alkenes formed, and we obtained 3-isopropyl-2,4-dimethyl-2-pentene without admixture of isomeric olefins.

$$(i\text{-}C_3H_7)_3\,COH \xrightarrow{+K} (i\text{-}C_3H_7)_3COK \xrightarrow{+CS_2} (i\text{-}C_3H_7)_3COCSSK \rightarrow$$
$$\xrightarrow{+C_2H_5\,I} (i\text{-}C_3H_7)_3\,COCSSC_2H_5 \xrightarrow{\sim 240^\circ} (i\text{-}C_3H_7)_2C{=}C\,(CH_3)_2 + SOC + C_2H_5SH$$

The reactions of diazoacetic ester with these alkenes were conducted at 100-110° (77° in the case of 2,3,3-trimethyl-1-butene); the alkene was taken in eightfold excess. In order to avoid isomerization of the olefin, in the case of 4-propyl-3-heptene and 3-isopropyl-2,4-dimethyl-2-pentene we used finely dispersed copper – so-called copper bronze – as catalyst. The absence of the isomerization of alkenes under the action of Cu or $CuSO_4$ in the course of their reaction with diazoacetic ester was established from their Raman spectra.

In the reactions of diazoacetic ester with 2,3,3-trimethyl-1-butene and with 4-propyl-3-heptene we isolated ethyl 2-t-butyl-2-methylcyclopropanecarboxylate (I) and ethyl 3-ethyl-2,2-dipropylcyclopropanecarboxylate (III) respectively in yields of 63 and 56%. In the case of 3-isopropyl-2,2-dimethyl-2-pentene, however, ethyl 2,2-diisopropyl-3,3-dimethylcyclopropanecarboxylate (V) was obtained in only about 14% yield. Since the electron density of the C=C bond in this alkene is clearly not less, and may be somewhat more, than in the isomeric 4-propyl-3-heptene (because of the larger number of methyl groups), which as we have shown earlier [1, 4] is of great importance in reactions with diazoacetic ester, such a low yield of (V) may be explained by the lower steric accessibility of the C=C bond in 3-isopropyl-2,4-dimethyl-2-pentene.

As in the previously prepared [1] ethyl 2-isopropyl-2-methylcyclopropanecarboxylate (from diazoacetic ester and 2,3-dimethyl-1-butene), in (III) and (V), as isolated from the reaction mixtures, we detected the presence of esters of unsaturated acids by the Raman spectra. The molecules of the olefins from which these esters were prepared each contain two reaction centers: in the case of 2,3-dimethyl-1-butene and 3-isopropyl-2,4-dimethyl-2-pentene these are the C=C bond and the bond between hydrogen and the tertiary carbon atom, and in the case of 4-propyl-3-heptene – the C=C bond and the bond between hydrogen and the carbon atom participating in the C=C bond. This makes it possible for reactions between these alkenes and the biradical: $CHCOOC_2H_5$ formed in the decomposition of diazoacetic ester to take two directions



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1235-1240, July, 1966. Original article submitted February 12, 1964.

The possibility of the formation of esters of unsaturated acids in accordance with the scheme (b) is confirmed by the fact of the withdrawal of hydrogen atoms by methyl and butoxyl radicals [5, 6] and also by the investigations of Doering and co-workers [7-9], who decomposed diazomethane and diazoacetic ester catalytically, thermally, and photochemically in saturated hydrocarbons (pentane, 2,3-dimethylbutane, cyclohexane, and cyclopentane) and isolated products of the addition of the biradicals $:CH_2$ and $:CHCOOC_2H_5$ at a C—H bond. In 3-isopropyl-2,4-dimethyl-2-pentene and 2,3-dimethyl-1-butene the hydrogen atoms attached to the tertiary carbon atoms are distinguished by low bond energy (high mobility), and this makes such a course of reaction still more probable. By the hydrolysis of (I) and (III) with aqueous-alcoholic NaOH we obtained the sodium salts of 2-t-butyl-2-methylcyclopropanecarboxylic acid (II) and 3-ethyl-2,2-dipropylcyclopropanecarboxylic acid (IV), by the reactions of which with CH_3Li in ether the corresponding methyl ketones were formed. By the reactions of (I) and (III) with CH_3MgCl we obtained alcohols, which according to the Raman spectrum contained unsaturated compounds as impurities, and these, according to their elemental compositions, were unsaturated alcohols probably arising as a result of the isomerization of the three-membered ring. The use of CH_3Li instead of CH_3MgCl enabled us to convert (I) and (III) into 2-t-butyl-α,α,2-trimethylcylcopropanemethanol and 3-ethyl-α,α-dimethyl-2,2-dipropylcyclopropanemethanol respectively without any unsaturated alcohol impurity.

Earlier [10] in the synthesis of α,α,2,2,3,3-hexamethylcyclopropanemethanol by the reaction of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate with CH_3MgBr we established that isomerization of the three-membered ring occurred. In our view, such isomerization is due to high strain in the ring caused by the presence of four methyl substituents on the carbon atoms forming the cyclopropane ring. In this case replacement of CH_3MgBr by CH_3MgCl made it possible to obtain only the unisomerized alcohol. However, in the present work the use of CH_3MgCl for the synthesis of α,α-dimethylcyclopropanemethanols from (I) and (III) proved inadequate as a measure to prevent the isomerization of the three-membered ring, which probably indicates the still higher strain in the rings of these esters.

EXPERIMENTAL

2,3,3-Trimethyl-1-butene was prepared from 2,3,3-trimethyl-2-butanol (synthesized by the Grignard reaction from 3,3-dimethyl-2-butanone and methylmagnesium bromide) by dehydration over iodine; b.p. 76.8-77.6° (750 mm); d_4^{20} 0.7053; n_D^{20} 1.4035. The literature [11] gives: b.p. 77.8° (760 mm); d_4^{20} 0.7050; n_D^{20} 1.4029.

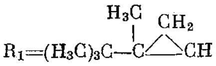
4-Propyl-3-heptene. 87 g of 4-propyl-4-heptanol, 15 g of toluene, and 3 g of iodine were introduced into a flask fitted with a reflux condenser and a Dean-Stark device. When the mixture had boiled for 30 min, 7.5 ml of water had separated. The olefin obtained was driven off and distilled three times over sodium through a rectifying column; b.p. 158.5-160.5° (740 mm); d_4^{20} 0.7502; n_D^{20} 1.4298. Found %: C 85.74, 85.96; H 14.44, 14.54; MR 48.18. $C_{10}H_{20}$. Calculated %: C 85.71; H 14.29; MR 48.06. The literature [11] gives: b.p. 161.2-163.2° (760 mm); d_4^{20} 0.7502; n_D^{20} 1.4291.

Raman spectrum ($\Delta\nu$, cm^{-1}): 816(2b); 873(2b); 893(3b); 930(3); 962(1); 1020(2b); 1037(3b); 1062(2b); 1100(3b); 1131(2b); 1172(1); 1200(1); 1225(2b); 1257(1); 1296(2b); 1333(1b); 1382(2b); 1452(5b); 1662(6); 2847(1b); 2876(5b); 2908(2b); 2935(3); 2963(3b).

3-Isopropyl-2,4-dimethyl-2-pentene. 66 g of carbon disulfide was added to the alkoxide prepared from 39 g of potassium and 158 g of 3-isopropyl-2,4-dimethyl-3-pentanol synthesized from isopropyllithium and 2,4-dimethyl-3-pentanone. The mixture was stirred for 1-1.5 h at 20° and diluted with ether, after which 180 g of ethyl iodide was added. The reaction mixture was then stirred for eight hours with heating, solvent was driven off, and from the residue was isolated 85 g of the xanthic ester $(i\text{-}C_3H_7)_3COCSSC_2H_5$; b.p. 80.5-81° (17 mm); d_4^{20} 0.8627; n_D^{20} 1.4490. Found MR 81.60. Calculated MR 80.74. The xanthic ester was distilled at a bath temperature of 240°. From the distillate, after rectification over sodium through a column we isolated 3-isopropyl-2,4-dimethyl-2-pentene; b.p. 78-79° (100 mm); d_4^{20} 0.7672; n_D^{20} 1.4385. Found %: C 85.71, 85.86; H 14.23, 14.20; MR 48.03. $C_{10}H_{20}$. Calculated %: C 85.63; H 14.37; MR 48.05.

Raman spectrum ($\Delta\nu$, cm^{-1}): 229(0); 305(2b); 331(2); 412(1); 443(1); 490(0); 507(1); 573(1); 609(1); 643(5); 680(1); 855(3); 918(4); 958(2); 1008(0); 1058(2b); 1095(2); 1120(2); 1160(1); 1189(1b); 1247(1b); 1323(2b); 1361(1); 1384(2b); 1440(5b); 1461(5b); 1657(8); 2868(8b); 2912(8b); 2925(8b); 2968(8b); 3047(4).

Ethyl 2-t-Butyl-2-methylcyclopropanecarboxylate $R_1COOC_2H_5$ (I)



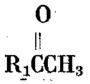
To a mixture of 300 g of 2,3,3-trimethyl-1-butene and 4 g of copper sulfate with stirring and boiling of the alkene a solution of 59 g of diazoacetic ester in 77 g of the alkene was added dropwise. At the end of the reaction excess of the alkene was driven off, and by rectification of the residue we isolated 60 g (63%) of (I); b.p. 78° (11 mm); d_4^{20} 0.9157; n_D^{20} 1.4412. Found %: C 71.06, 71.03; H 10.72, 10.73; MR 53.07. $C_{11}H_{20}O_2$. Calculated %: C 71.63; H 10.94; MR 53.46.

Raman spectrum ($\Delta\nu$, cm^{-1}): 267 (0); 382 (1); 442 (0); 530 (1); 575 (1); 608 (2); 624 (10); 764 (3b); 818 (1); 848 (3); 858 (2b); 872 (3); 913 (1b); 927 (5); 959 (2b); 1002 (1b); 1023 (3); 1043 (2); 1080 (2); 1110 (1b); 1173 (1b); 1198 (1b); 1276 (1b); 1292 (2b); 1386 (2b); 1403 (2b); 1452 (2b); 1473 (2b); 1737 (3); 2884 (3); 2919 (4); 2941 (2b); 2995 (6); 3015 (4); 3080 (2).

2-t-Butyl-2-methylcyclopropanecarboxylic Acid R_1COOH (II)

The sodium salt of the acid (II), prepared by the hydrolysis of (I) with 20% aqueous-alcoholic NaOH for about 20 h with heating, was treated with 5% H_2SO_4. (II) was extracted with ether and distilled; b.p. 120-122° (6 mm); m.p. 61°. Acid value: found 157.21; calc. 156.22.

2-t-Butyl-2-methylcyclopropyl Methyl Ketone

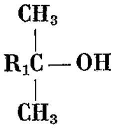


$R_1\overset{\overset{O}{\|}}{C}CH_3$

The sodium salt of the acid (II), prepared from NaOH and 31 g of (II), was added to CH_3Li prepared in ether from CH_3Cl and 3.5 g of lithium. The mixture was heated for 14 h in a water bath and then decomposed with water. We obtained 14 g (50.5%) of the ketone; b.p. 63° (7 mm); d_4^{20} 0.8698; n_D^{20} 1.4452. Found %: C 77.40, 77.67; H 11.60, 11.60; MR 47.21. $C_{10}H_{18}O$. Calculated %: C 77.86; H 11.76; MR 47.20. Semicarbazone, m.p. 198-199° (decomp., from alcohol). Found %: N 20.42, 20.39. $C_{11}H_{21}ON_3$. Calculated %: N 19.89.

Raman spectrum ($\Delta\nu$, cm^{-1}): 500 (1); 545 (1); 580 (2); 603 (4); 648 (3); 760 (3); 778 (2); 830 (4); 905 (2); 924 (3); 962 (1b); 1030 (1); 1070 (1); 1168 (1b); 1205 (3); 1277 (1b); 1383 (1b); 1438 (3b); 1456 (2b); 1693 (2); 2875 (2); 2916 (3b); 2967 (5b); 3075 (1).

2-t-Butyl-α,α,2-trimethylcyclopropanemethanol

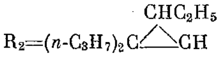


$R_1\underset{CH_3}{\overset{CH_3}{C}}—OH$

A solution of 30 g of (I) in ether was added dropwise to an ethereal solution of CH_3Li prepared from 5 g of Li and CH_3Cl. The mixture was heated in a water bath and then decomposed with water. We isolated 24 g (87%) of the alcohol; b.p. 82° (16 mm); d_4^{20} 0.8736; n_D^{20} 1.4536. Found %: C 77.30, 77.00; H 12.80, 12.73; MR 52.73. $C_{11}H_{22}O$. Calculated %: C 77.58; H 13.02; MR 53.15.

Raman spectrum ($\Delta\nu$, cm^{-1}): 276 (1b); 330 (0); 387 (1b); 412 (1b); 450 (1b); 544 (2); 550 (1); 582 (2); 602 (7); 653 (4); 660 (3); 702 (3); 726 (1); 785 (1); 807 (3); 852 (9); 882 (2); 910 (2); 927 (6); 951 (1b); 960 (1b); 1022 (1b); 1041 (2b); 1066 (1b); 1105 (1b); 1155 (1b); 1192 (1b); 1208 (3); 1257 (2); 1300 (1); 1320 (2b); 1401 (3b); 1447 (6b); 1465 (6b); 2875 (4); 2916 (6); 2870 (10); 2992 (8b); 3075 (2).

Ethyl 3-Ethyl-2,2-dipropylcyclopropanecarboxylate $R_2COOC_2H_5$ (III)



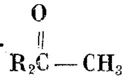
By the reaction of 300 g of 4-propyl-3-heptene and 34 g of diazoacetic ester at 100-110° in presence of a catalytic amount of copper bronze we obtained 36 g (56%) of (III), which according to the Raman spectrum contained some unsaturated ester as impurity, which was then removed by treatment with 0.25% $KMnO_4$ solution at about 20°; b.p. 116° (11 mm); d_4^{20} 0.8945; n_D^{20} 1.4435. Found %: C 73.78, 73.82; H 11.52, 11.42; MR 67.16. $C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.57; MR 67.40.

Raman spectrum ($\Delta\nu$, cm^{-1}): 696 (1b); 823 (0); 900 (2b); 952 (1b); 1036 (2b); 1045 (2b); 1092 (3b); 1110 (4b); 1167 (1); 1212 (2); 1255 (0); 1302 (1); 1372 (1); 1432 (4b); 1447 (5b); 1718 (1); 2867 (6); 2922 (5); 2935 (5); 2965 (4b); 2982 (2).

3-Ethyl-2,2-dipropylcyclopropanecarboxylic Acid R_2COOH (IV)

This was prepared by treating the sodium salt of the acid (IV) with 5% H_2SO_4; b.p. 142-143° (5 mm); d_4^{20} 0.9341; n_D^{20} 1.4580. Found: MR 57.92; acid value 198.83. $C_{12}H_{22}O_2$. Calculated: MR 57.91; acid value 198.30.

3-Ethyl-2,2-dipropylcyclopropyl Methyl Ketone

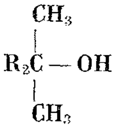


$$R_2\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$

17 g of the sodium salt of the acid (IV) was added to CH_3Li prepared in ether from CH_3Cl and 2 g of lithium. The mixture was heated for 14 h in a water bath and then decomposed from water. We obtained 9 g (59.5%) of the ketone; b.p. 82.5° (5 mm); d_4^{20} 0.8596; n_D^{20} 1.4495. Found %: C 79.26, 79.43; H 12.10, 12.10; MR 61.31. $C_{13}H_{24}O$. Calculated %: C 79.52; H 12.32; MR 61.14. Semicarbazone, m.p. 148°. Found %: N 16.99, 16.69. $C_{14}H_{27}ON_3$. Calculated %: N 16.58.

Raman spectrum ($\Delta\nu$, cm^{-1}): 622 (1); 721 (1b); 755 (2); 798 (2b); 862 (2b); 892 (2b); 933 (1); 951 (1); 978 (1b); 1035 (1b); 1084 (1b); 1103 (1b); 1213 (2); 1266 (1); 1292 (1); 1351 (1); 1447 (5b); 1691 (3b); 2873 (5); 2915 (8); 2937 (1b); 2970 (3); 3075 (5).

3-Ethyl-α,α-dimethyl-2,2-dipropylcyclopropanemethanol

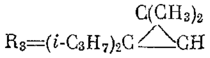


$$R_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—OH$$

An ethereal solution of 29 g of (III) was added dropwise to an ethereal solution of CH_3Li prepared from 4.2 g of lithium and CH_3Cl. The mixture was heated for 15 h in a water bath and then decomposed with water. We obtained 22 g (81%) of the alcohol; b.p. 104.5° (9 mm); d_4^{20} 0.8604; n_D^{20} 1.4510. Found: MR 66.46. Calculated: MR 67.10.

Raman spectrum ($\Delta\nu$, cm^{-1}): 292 (2b); 608 (1); 728 (2b); 768 (1b); 786 (1b); 833 (4b); 876 (4); 901 (5); 956 (4); 996 (0); 1045 (3b); 1095 (3b); 1125 (3b); 1178 (0); 1235 (1); 1270 (1); 1298 (2); 1382 (1); 1440 (6b); 1460 (6b); 1660 (0); 2847 (6); 2890 (4); 2918 (3); 2950 (5); 3075 (1).

Ethyl 2,2-Diisopropyl-3,3-dimethylcyclopropanecarboxylate $R_3COOC_2H_5$ (V)



A solution of 7 g of diazoacetic ester in an equal amount of 3-isopropyl-2,4-dimethyl-2-pentene was added dropwise with stirring to a mixture of 70 g of the same alkene and 1 g of copper bronze at 95-105°. When reaction was complete excess of the alkene was distilled off. As a result of two similar experiments we obtained 4 g (14.4%) of product; b.p. 101-122° (12 mm); d_4^{20} 1.0072; n_D^{20} 1.4450; according to the Raman spectrum unsaturated esters were present as impurity. After treatment with 0.25% aqueous $KMnO_4$ solution at about 20°, extraction with ether, and distillation we obtained a product having: b.p. 106-115° (12 mm); d_4^{20} 0.9319; n_D^{20} 1.4530.

Raman spectrum* ($\Delta\nu$, cm^{-1}): 232 (0); 254 (0); 271 (0); 290 (0); 325 (0); 319 (0); 383 (0); 415 (0); 618 (2); 685 (0); 739 (1); 776 (0); 841 (3); 876 (3); 898 (0); 939 (1); 961 (0); 1023 (0); 1115 (2b); 1303 (0); 1418 (0); 1449 (3b); 1475 (2b); 1509 (0); 1535 (1); 1724 (2); 2872 (3); 2931 (3b); 2974 (3b); 3022 (0); 3045 (2); 3075 (1); 3099 (1); 3122 (3).

2,2-Diisopropyl-3,3-dimethylcyclopropanecarboxylic Acid R_3COOH

(V) was hydrolyzed with 10% alcoholic KOH for 20-25 h, and then the above-named acid was isolated; m.p. 154-155° (alcohol). Found %: C 72.56, 72.63; H 11.37, 11.22; acid value 196.64. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.18; acid value 198.30.

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* The spectrum was determined by E. M. Popov and G. M. Andrianova of the Optical Laboratory.

CONCLUSIONS

1. An investigation was made of the reactions of diazoacetic ester with the branched alkenes 2,3,3-trimethyl-1-butene, 4-propyl-3-heptene, and 3-isopropyl-2,4-dimethyl-2-pentene.

2. In the synthesis of alcohols from ethyl 2-t-butyl-2-methylcyclopropanecarboxylate and ethyl 3-ethyl-, 2,2-dipropylcyclopropanecarboxylate opening of the cyclopropane ring occurs to some extent under the action of CH_3MgCl under the conditions of the Grignard reaction.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
