For repeated use of the catalyst the solution over the catalyst was poured off, the catalyst washed with hexane and dried in vacuum at ~20°. Complete removal of reaction products was checked by GLC. The catalyst so regenerated was used again for disproportionation by the method described.

CONCLUSIONS

1. By polymerizing various monomers in the presence of transition-metal salts (e.g., WCl_6) and a Grignard reagent, disproportionation catalysts containing a carbochain polymeric support have been obtained. Lewis acids were used as cocatalysts for the disproportionation of the olefins.

2. The activity and selectivity in the action of the catalytic systems obtained have been studied as a function of the nature of the cocatalyst, the ratio of the components, and the nature of the solvent in the disproportionation of 2-pentene.

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ACYLATION OF NORCARANE AND ITS DERIVATIVES BY PIVALOYL TETRAFLUOROBORATE*

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Cationic complexes of the acyl tetrafluoroborate type were studied earlier in the acylation reactions of alkenes [2, 3] and alkynes [4, 5]. The purpose of the present investigation was to determine the possibility of using these reagents for the acylation of cyclopropane derivatives. Norcarane (I) and also 1-methyl- and 1-phenylnorcaranes (II, III) were chosen as subjects for investigation.

As found, the reaction of compound (I) with pivaloyl tetrafluoroborate (IV) takes place fairly rapidly and fully even at −50°C. Subsequent treatment of the reaction mass with water leads to a mixture of products (V)-(IX) with an overall yield of 60-75%.

* For preliminary report see [1].

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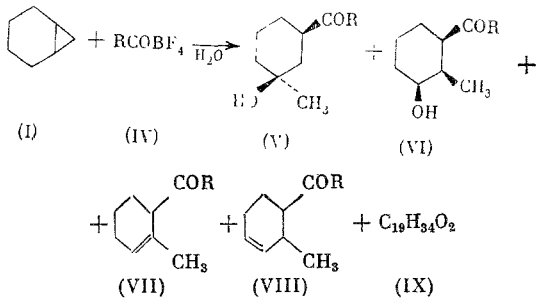
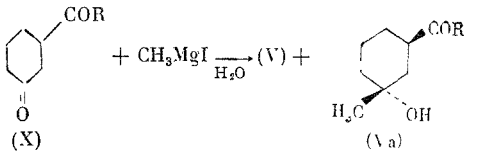


Here and subsequently $R = C(CH_3)_3$.

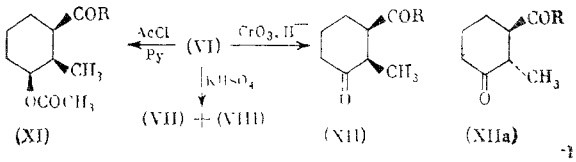
The ratio of the components in the mixture depends substantially on the acylation conditions. Thus, during decomposition of the mixture obtained from (I) and (IV) in a 1:1 mixture of CH_2Cl_2 and $C_2H_4Cl_2$ by water at −50°C compounds (V) and (VII) are mainly formed (with yields of 39 and 22%, respectively), whereas analogous treatment of the reaction complex obtained in CH_3NO_2 at −25°C gives mainly compounds (VI) and (VII) (with yields of 36 and 13%, respectively).

The structures of the products (V)-(VIII) were proved by spectrometry and by alternative syntheses. The hydroxy ketone (V) was obtained by the action of methylmagnesium iodide on the diketone (X). Apart from compound (V), the epimeric hydroxy ketone (Va) is also formed in this reaction.



According to the IR spectra, in compound (V) there is a strong intramolecular hydrogen bond ($\Delta\nu$ 160 cm^{-1}), which is not detected in compound (Va). It can therefore be supposed that compound (V) is the isomer with the cis arrangement of the OH and COR groups, while compound (Va) is the isomer with the trans arrangement of these substituents. Consequently, compound (Va) must be the more stable isomer, since the realization of the most stable conformation with the cis-1,3-diequatorial arrangement of the bulky CH_3 and $COC(CH_3)_3$ groups is only possible for (Va). In fact, data on the alkaline equilibrium epimerization of the individual compounds (V) and (Va) showed considerably greater stability for the latter; at 64°C the equilibrium ratio of (V) to (Va) is 1:2.7.

The other hydroxy ketone formed in considerable amounts during the experiments in nitromethane was found to be the 1,2,3-cis-syn-cis derivatives of cyclohexane (VI). The 1,2,3 position of the substituents in (VI) follows from analysis of the PMR spectrum of its acetate (XI). The vicinal arrangement of the ring methine H atoms in the CHOCOMe (δ 4.73 ppm), CHMe (2.29 ppm), and CHCOR (3.0 ppm) groups was demonstrated by double resonance. Dehydration of (VI) by the action of $KHSO_4$ leads to a mixture of two unsaturated ketones (VII) and (VIII), the structure of which follows from their IR and PMR spectra, and this also confirms the adopted position for the substituents in (VI). The cis arrangement of the OH and COR groups in compound (VI) follows from the presence of a strong intramolecular hydrogen bond in it ($\Delta\nu$ 200 cm^{-1}). To determine the relative configuration of the CH_3 and COR groups the hydroxy ketone (VI) was converted into the diketone (XII), from which the isomer (XIIa) was obtained under conditions of alkaline epimerization. On the attainment of equilibrium the ratio of (XII) to (XIIa) was 1:5.7.



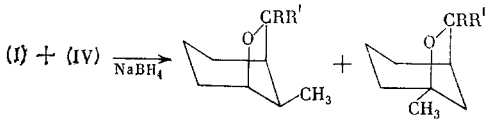
On this basis it was assumed that (XIIa) is the more stable trans-diequatorial isomer, and the CH_3 and COR groups in (XII) and, consequently, in the hydroxy ketone (VI) are in the cis configuration.

The structure of the β,γ- and γ,δ-unsaturated ketones (VII) and (VIII) (1:1.3) follows from the IR and PMR spectra and also from the above-mentioned fact that they are formed during dehydration of (VI). Among the ketones obtained in the reaction of (I) with (IV) a small amount (3-5%) of unsaturated ketones (GLC), cor-

responding to the products from dehydration of the hydroxy ketone (V) by the action of $POCl_3$ in pyridine, was found.

In addition to the above-mentioned products (V)-(VIII), a certain amount of heavier difficultly distilled substances is formed in the reaction of (I) with (IV). Among them we identified the hydroxy ketone (IX), the composition of which corresponded to the product from the reaction of one equivalent of $(CH_3)_3CCO^+$ with two molecules of (I) (IR, PMR, and mass spectra).

Since the acylation itself of compound (I) is carried out under conditions excluding the presence of moisture, the formation of the hydroxy ketones (V) and (VI) consequently takes place as a result of reaction of the reaction complex with the nucleophile (water) introduced to decompose this complex. It can therefore be expected that change in the character of the nucleophile will lead to a change in the nature of the isolated products. In fact, if the reaction complex obtained by the reaction of (I) with (IV) in nitromethane [i.e., giving a mixture of (V)-(VIII) during treatment with water] is treated with a hydride-ion donor such as $NaBH_4$ or $(C_4H_9)_3SnH$, the main isolated compound is a derivative of oxabicyclooctane (XIII) (yield 35%). During analogous treatment of the reaction products in the $CH_2Cl_2-C_2H_4Cl_2$ medium, 20% of compound (XIII) an l 36% of compound (XIV) (IR, PMR, and mass spectra) were obtained.

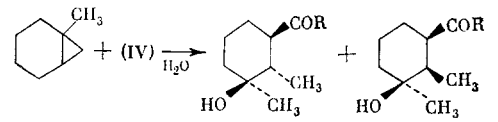


(XIII), (XIIIa) (XIV), (XIVa)

R′ = H (XIII), (XIV); D (XIIIa), (XIVa)

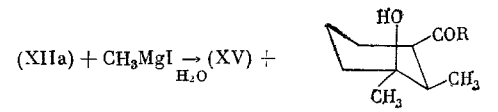
The use of deuterated compounds such as $(n\text{-}C_4H_9)_3SnD$ as the source of the nucleophile led to the formation of (XIIIa) and (XIVa) in the PMR spectrum of which the corresponding signals at 3.66 ppm for (XIIIa) and 3.55 ppm for (XIVa) were absent.

The acylation of compound (II) by the action of compound (IV) in the $CH_2Cl_2-C_2H_4Cl_2$ medium at −35°C, followed by treatment with an aqueous solution of sodium bicarbonate, gave the hydroxy ketones (XV) and (XIV) (overall yield 50-55%, ratio 4 : 1) as the main products.



(II) (XV) (XVI)

The structure of (XV) as the 1,2,3 derivative of cyclohexane with the trans arrangement of the CH_3 group at 2-C and the COR group at 3-C was demonstrated by the production of this compound by the reaction of methylmagnesium iodide with the diketone (XIIa) (with the trans-diequatorial arrangement of the substituents). However, the main product in this alternative synthesis is not (XV) but the epimeric hydroxy ketone (XVa) (in a ratio of 1 : 4.5).

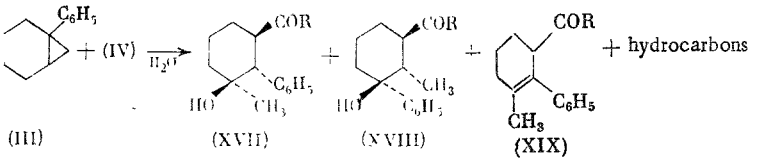


(XVa)

The preferential formation of compound (XVa) shows that it is the epimer with an axial OH group, since it is known [6] that axial alcohols are the main products from the Grignard reaction in the case of conformationally fixed cyclohexanones. Thus, the hydroxy ketone (XV) is the isomer with the equatorial arrangment of the OH, CH_3, and COR groups.

In the hydroxy ketone (XVI) the COR and CH_3 groups at 2-C are in the cis configuration, as follows from the fact that this product is formed with a yield of ~80% in the Grignard reaction with the cis-diketone (XII). This makes it possible to propose the axial configuration for the OH group, and this is consistent with the IR data, which indicate the presence of a strong intramolecular hydrogen bond in compound (XVI) ($\Delta\nu$ 190 cm^{-1}). It should be noted that the isomeric hydroxy ketone (XV) also contains the OH and COR groups in the cis configuration, but bands for an intramolecular hydrogen bond are not found in its IR spectrum. This is due to the fact that the formation of an intramolecular hydrogen bond in this case must inavoidably involve conformational inversion, leading to the unfavorable axial orientation of the CH_3 group at 2-C.

The reaction of compound (III) with compound (IV) at −30°C in the $CH_2Cl_2-CH_3NO_2$ medium (2:1) gave, after treatment with water, three acylation products, i.e., the hydroxy ketones (XVII) and (XVIII) and the unsaturated ketone (XIX) in ratios of 4:1:2.5 (overall yield ~45%). In addition, the reaction products contained about 40% of a hydrocarbon mixture consisting of (III), hydrocarbons with the composition $C_{13}H_{18}$, and high-molecular-weight hydrocarbons.



(III) (XVII) (XVIII) (XIX)

The structure of the hydroxy ketone (XVII), which is the main reaction product, was proved largely by the spectral data. Thus, analysis of the PMR spectrum of (XVII), recorded in the presence of $Eu(DPM)_3$, showed that the benzyl proton at 2-C gives a doublet with J = 11.4 Hz, while the vicinal proton at 3-C gives a triplet of doublets with J = 11.4 and 3.5 Hz. From this it follows that the COR and C_6H_5 groups have the trans-diequatorial arrangement. The question of the configuration of the OH group cannot be considered finally solved, but by analogy with other hydroxy ketones formed during acylation of norcarane and its analogs it can be supposed that the hydroxy group has the cis configuration in relation to the COR group.

The structure and stereochemistry of the hydroxy ketone (XVIII) were proved by alternative synthesis from the trans-diketone (XIIa) and phenylmagnesium bromide and also by the IR data (the presence of an intramolecular hydrogen bond). The unsaturated ketone (XIX) was identified by the PMR spectra and also by the fact that it is formed during the acid dehydration of hydroxy ketone (XVII).

The question of the mechanism of the opening of the cyclopropane ring in the described reactions proved fairly complex, and its solution requires further investigation with the use of labeled derivatives.

EXPERIMENTAL

Pivaloyl tetrafluoroborate (IV) was generated directly in the reaction mass by the addition of pivaloyl chloride to a solution of an equimolar amount of $AgBF_4$. Compounds (I)-(III) were prepared by the method in [7]. The GLC analysis was performed on an LKhM-8MD chromatograph with a katharometer or flame-ionization detector (200-300 × 0.25 cm columns, 5% SKTFT-50Kh on Chromosorb G, 5% SE-30 on Chromaton N-AW-DMCS, 15% Reoplex-400 on Chromaton N-AW-DMCS, helium). The PMR spectra were recorded on a DA-60-IL instrument (60 MHz) with TMS as internal standard; the chemical shifts are given on the δ scale; the signals were assigned by analogy with published data [8] and in accordance with their integral intensity, and in a number of cases double resonance was used to assign the signals and determine the spin−spin coupling constants. The IR spectra were recorded on a UR-20 instrument in carbon tetrachloride solution at a concentration of ~0.1 M and again with a concentration of ~0.003 M for the hydroxyl-containing compounds [9].

Acylation of Norcarane (I). Method A. To a solution of 2.54 g (13 mmole) of $AgBF_4$ in a 1:1 mixture of CH_2Cl_2 and $C_2H_4Cl_2$ at −50°C we added a solution of 0.96 g (10 mmole) of (I) and 1.56 g (13 mmole) of pivaloyl chloride in 5 ml of methylene chloride. The mixture was stirred at this temperature for 10 min and decomposed with a suspension of ice and sodium bicarbonate in cooled methylene chloride. After drying and distillation of the solvents, according to GLC data [SKTFT-50Kh, 170°C, with (Va) as internal standard], the residue contained 39% of 1-methyl-3-pivaloylcyclohexanol (V), 22% of 1-methyl-6-pivaloylcyclohexene (VII), and 10% of 3-methyl-4-pivaloylcyclohexene (VIII).

Method B. To a solution of 2.54 g (13 mmole) of $AgBF_4$ in 20 ml of nitromethane at −25°C we added a solution of 0.96 g (10 mmole) of (I) and 1.56 g (13 mmole) of pivaloyl chloride in 5 ml of nitromethane. The temperature was then raised to 0°C, and the mixture was kept for 10 min and treated in the usual way. After removal of the solvents 2.0 g of residue was obtained. According to GLC, it contained 36% of 2-methyl-3-pivaloylcyclohexanol (VI), 13% of compound (VII), 6% of compound (V), and 10% of the dimeric hydroxy ketone $C_{19}H_{34}O_2$.

The hydroxy ketone (V) was isolated in the pure form by preparative TLC (silica gel L, 40-100 μ, 1.5:1:1 ether−benzene−heptane, R_f ~ 0.18), mp 53-54°C. Found %: C 71.91; H 11.28. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.19. IR spectrum (ν, cm^{-1}): 3611 w, 3440 (OH, intramolecular hydrogen bond), 1702 (C=O). PMR spectrum: 1.11 s [9H, $C(CH_3)_3$]; 1.16 s (3H, CH_3); 2.8-3.1 m (1H, CHCO); 3.15 s (1H, OH). Mass spectrum, m/e: 183 $(M - CH_3)^+$, 180 $(M - H_2O)^+$, 141 $(M - C_4H_9)^+$, 123 $(M - C_4H_9 - H_2O)^+$.

The hydroxy ketone (VI) was also isolated by preparative TLC (silica gel L, 40-100 μ, 1:1:1.5 ether–benzene–hexane, $R_f \sim 0.22$), mp 58.5-60°C. Found %: C 72.27; H 11.06. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.19. IR spectrum (ν, cm^{-1}): 3629 w, 3430 (OH, intramolecular hydrogen bond), 1691 (C=O). PMR spectrum: 0.80 d (3H, CH_3, J=7 Hz); 1.11 s [9H, $C(CH_3)_3$]; 3.11 m (1H, CHCO); 3.52 m (1H, CHO); 4.22 s (1H, OH). Mass spectrum, m/e: 180 $(M - H_2O)^+$, 141 $(M - C_4H_9)^+$, 123 $(M - C_4H_9 - H_2O)^+$.

The unsaturated ketone (VII) was isolated in the pure form by preparative GLC (Reoplex 400, 175°C) after distillation of the reaction mixture (or the residue from the preparative plate) under vacuum. A fraction boiling at 65-70°C (1 mm Hg) was obtained. Found %: C 79.25; H 10.92. $C_{12}H_{20}O$. Calculated %: C 79.91; H 11.11. IR spectrum (ν, cm^{-1}): 1700 (C=O), 1670, 3040 (C=CH). PMR spectrum: 1.11 s [9H, $C(CH_3)_3$]; 1.41 (3H, CH_3); 3.5 m (1H, CHCO); 5.5 m (1H, C=CH).

The dimeric hydroxy ketone $C_{19}H_{34}O_2$ was isolated by preparative TLC under the same conditions as (VI) ($R_f \sim 0.45$), mp 83-84°C. IR spectrum (ν, cm^{-1}): 3410 (OH), 1686 (C=O). PMR spectrum: 1.20 s [9H from total protons, $C(CH_3)_3$]. Mass spectrum, m/e: 294 w $(M)^+$, 279 w $(M - CH_3)^+$, 276 $(M - H_2O)^+$, 237 $(M - C_4H_9)^+$, 219 $(M - C_4H_9 - H_2O)^+$, 191 $(M - COC_4H_9 - H_2O)^+$.

Epimerization of (V). A solution of 0.4 g of hydroxy ketone (V) in 7 ml of methanol with the addition of 0.1 g of sodium methoxide was boiled for 3 h. After the usual treatment and removal of the solvent 0.39 g of a residue was obtained. It consisted of a 1:2.7 mixture of (V) and (Va) (GLC, SKTFT-50Kh, 170°C). By preparative TLC (silica gel L, 40-100 μ, 1.5:1:1 ether–benzene–hexane, $R_f \sim 0.26$) 0.28 g (70%) of 1-methyl-3-pivaloylcyclohexanol (Va) was obtained; mp 58.5-60°C. Found %: C 72.31; H 11.25. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.19. IR spectrum (ν, cm^{-1}): 3620 (OH), 1706 (C=O). PMR spectrum: 1.11 s [9H, $C(CH_3)_3$]; 1.16 s (3H, CH_3); 3.15-3.45 (2H, CHCO, and OH). Mass spectrum, m/e: 198 $(M)^+$, 183 $(M - CH_3)^+$, 180 $(M - H_2O)^+$, 141 $(M - C_4H_9)^+$, 123 $(M - C_4H_9 - H_2O)^+$, 113 $(M - COC_4H_9)^+$. The reverse epimerization of compound (Va) under analogous conditions also gives a mixture of isomers in a ratio of 2.7:1.

Alternative Synthesis of (V) and (Va). To a solution of methylmagnesium bromide (from 0.16 g of magnesium) we added 0.55 g (3 mmole) of 3-pivaloylcyclohexanone (X) in 5 ml of ether. The mixture was stirred for 5 min and decomposed with dilute hydrochloric acid. After distillation of the ether the residue was separated by preparative TLC as described above. A 0.27-g yield (45%) of the hydroxy ketone (V) and 0.21 g (40%) of the isomer (Va) were obtained. Their identity with the previously obtained compounds was confirmed by GLC, TLC, and IR spectra.

Acylation of (VI). To a solution of 0.7 g (3.5 mmole) of (VI) in 5 ml of pyridine, while stirring and cooling with ice, we added dropwise 1 ml of acetyl chloride. After 2 h the mixture was poured into ice and extracted with ether. After distillation of the ether the residue was distilled under vacuum. A 0.78-g yield (90%) of 2-methyl-3-pivaloylcyclohexyl acetate (XI) was obtained; bp 100-101°C (1 mm Hg). Found %: C 70.43; H 9.94. $C_{14}H_{24}O_3$. Calculated %: C 69.97; H 10.06. IR spectrum (ν, cm^{-1}): 1702 (C=O), 1738 (OC=O). PMR spectrum: 0.79 d (3H, CH_3, J ~ 7 Hz); 1.11 s [9H, $C(CH_3)_3$]; 1.97 s (3H, CH_3); 2.3 m (1H, CHC); 3.0 m (1H, CHCO); 4.7 m (1H, CHO). Mass spectrum, m/e: 240 w $(M)^+$, 183 $(M - C_4H_9)^+$, 180 $(M - CH_3COOH)^+$.

Oxidation (VI). To a solution of 0.5 g (5 mmole) of chromic anhydride and 0.6 g of sulfuric acid in 10 ml of water we added a solution of 0.78 g (4 mmole) of (VI) in 3 ml of acetone. The mixture was stirred for 30 min. It was then decomposed with water, extracted with ether, and dried with sodium sulfate. After distillation of the solvents 0.73 g (90%) of cis-2-methyl-3-pivaloylcyclohexanone (XII) was obtained; mp 83.5-84°C. Found %: C 72.97; H 9.98. $C_{12}H_{20}O_2$. Calculated %: C 73.45; H 10.20. IR spectrum (ν, cm^{-1}): 1709, 1723 (C=O). PMR spectrum: 0.83 d (3H, CH_3, J ≈ 7 Hz); 1.11 s [9H, $C(CH_3)_3$]; 2.0-2.5 (3H, CH_2COCH); 3.69 m (1H, CHCOR).

Epimerization of Diketone (XII). A solution of 0.26 g of (XII) in 6 ml of methanol with the addition of 0.2 g of sodium methoxide was boiled for 4 h. After the usual treatment and removal of the solvent 0.26 g of a crystalline substance was obtained. According to GLC (SKTFT-50Kh, 180°C), it contained 15% of the initial cis-diketone (XII) and 85% of the trans isomer (XIIa). The latter was isolated in the pure form by preparative TLC (silica gel LS, 5-40 μ, 1:1:1 ether–benzene–hexane, $R_f \sim 0.45$; for the initial cis-diketone $R_f \sim 0.3$); mp 47-48°C. Found %: C 73.67; H 10.24. $C_{12}H_{20}O_2$. Calculated %: C 73.45; H 10.20. PMR spectrum: 0.75 d (3H, CH_3, J ≈ 7 Hz); 1.11 s [9H, $C(CH_3)_3$]; 2.6-3.0 m (1H, CHCOR). The reverse epimerization led to the same mixture of isomers.

Dehydration of the Hydroxy Ketone (VII). A mixture of 0.5 g (2.5 mmole) of (VI) with 0.5 g (3.7 mmole) of $KHSO_4$ (calcined at 300°C) was heated at 170°C for 5 min and cooled. A solution of potassium carbonate was

added, and the mixture was extracted with ether. After removal of the solvent 0.4 g (90%) of a residue was obtained, according to GLC (Reoplex-400, 150°C), it contained two products, one of which was the unsaturated ketone (VII) discussed above. The second compound, which was isolated by preparative GLC, was the γ,δ-unsaturated ketone (VIII). IR spectrum (ν, cm^{-1}): 1698 (C=O), 1657, 3024 (CH=CH). PMR spectrum: 0.80 d (3H, CH_3, J≈ 7 Hz); 1.11 s [9H, $C(CH_3)_3$]; 3.0 m (1H, CHCO); 5.55 m (2H, CH=CH).

Production of 6-Oxabicyclo[3.2.1]octane Derivatives. The acylation of (I) was carried out as described above, but the reaction mixture was decomposed by the addition of sodium borohydride with stirring for 1 h. After the usual treatment the residue was distilled under vacuum, and the fraction boiling at 70-80°C (7 mm Hg) was collected. In this way the reaction in a 1:1 mixture of CH_2Cl_2 and $C_2H_4Cl_2$ at −50°C gave 36% of 5-methyl-7-tert-butyl-6-oxabicyclo[3.2.1]octane (XIV) and 20% of 8-methyl-7-tert-butyl-6-oxabicyclo[3.2.1]-octane (XIII), and reaction in nitromethane at −20°C gave 35% of (XIII) and 7% of (XIV). The isomers were separated by preparative GLC (Reoplex-400, 160°C) or by preparative TLC [silica gel LS, 5-40 μ, 4:1 hexane−ether, R_f ~ 0.4 for (XIII) and ~0.5 for (XIV)]. In the IR spectra of both isomers there are no frequencies in the region of 1500-1800 and 3000-3600 cm^{-1}. PMR spectrum (XIII): 0.98 d (3H, CH_3, J≈ 7 Hz); 1.0 s [9H, $C(CH_3)_3$]; with the addition of $Eu(DPM)_3$ or $Eu(fod)_3$ the $C(CH_3)_3$ signal was shifted downfield more strongly than the CH_3 signal; 3.66 d (1H, CHRO, J=2.8 Hz); 3.89 (1H, CHO). Mass spectrum (III), m/e: 1.82 $(M)^+$, 125 $(M - C_4H_9)^+$, 107 $(M - C_4H_9 - H_2O)^+$; mass spectrum (XIIIa): 1.83 $(M)^+$, 126 $(M - C_4H_9)^+$. Found %: C 78.39; H 12.18. $C_{12}H_{22}O$. Calculated %: C 79.06; H 12.16. PMR spectrum (XIV): 0.98 s [9H, $C(CH_3)_3$]; 1.20 s (3H, CH_3); 3.55 d (1H, CHRO, J=2.7 Hz).

Acylation of 1-Methylnorcarane (II). To a solution of 2.54 g (13 mmole) of $AgBF_4$ in a 1:2 mixture of CH_2Cl_2 and $C_2H_4Cl_2$ at −35°C we added a solution of 1.1 g (10 mmole) of (II) and 1.56 g (13 mmole) of pivaloyl chloride in 5 ml of methylene chloride. The mixture was stirred for 20 min and decomposed with a mixture of ice and sodium carbonate. After the usual treatment the residue was separated by preparative TLC (aluminum oxide, 1:1:1 ether−benzene−hexane). A 0.78-g yield (37%) of 1,2-dimethyl-3-pivaloylcyclohexanol (XV) was obtained; R_f ~ 0.25, mp 50-51°C. Found %: C 73.16; H 11.24. $C_{13}H_{24}O_2$. Calculated %: C 73.54; H 11.43. IR spectrum (ν, cm^{-1}): 3612 (OH), 1704 (C=O). PMR spectrum: 0.72 d (3H, CH_3 at 2-C, J≈ 7 Hz); 1.10 s [9H, $C(CH_3)_3$]; 1.04 s (3H, CH_3) [the addition of $Eu(DPM)_3$ shifts this signal downfield]; 2.67 m (1H, CHCO); 3.25 s (1H, OH). Mass spectrum, m/e: 212 $(M)^+$, 197 $(M - CH_3)^+$, 194 $(M - H_2O)^+$, 155 $(M - C_4H_9)^+$, 137 $(M - C_4H_9 - H_2O)^+$. A 0.20-g yield (9%) of the hydroxy ketone (XVI) was also obtained; R_f ~ 0.4. IR spectrum (ν, cm^{-1}): 3621, 3430 (OH); 1692, 1702 (C=O, intramolecular hydrogen bond). PMR spectrum: 0.85 d (3H, CH_3 at 2-C, J≈ 7 Hz); 1.10 s (3H, CH_3); 1.15 s [9H, $C(CH_3)_3$]; 3.35 m (1H, CHCO); 5.06 s (1H, OH).

Alternative Synthesis of (XV) and (XVII). To methylmagnesium bromide in ether we added an equimolar amount of the cis-diketone (XII). The mixture was treated in the usual way, and ~80% of the hydroxy ketone (XVI) was obtained. Similarly from trans-diketone (XIIa) and methylmagnesium bromide we obtained 15% of the hydroxy ketone (XV) and 65% of the hydroxy ketone (XVa); mp 64.5-66°C. IR spectrum (ν, cm^{-1}): 3620 (OH), 1700 (C=O). PMR spectrum: 0.75 d (3H, CH_3 at 2-C, J≈ 7 Hz); 1.13 s [9H, $C(CH_3)_3$]; 1.20 s (3H, CH_3); 3.07 td (1H, CHCO, J_{aa} ≈ 11, J_{ae} ≈ 4 Hz); the signal of the OH group is in the region of the methylene protons.

Acylation of 1-Phenylnorcarane (III). To a solution of 2.54 g (13 mmole) of $AgBF_4$ in a 2:1 mixture of CH_2Cl_2 and CH_3NO_2 at −30°C we added a solution of 1.72 g (10 mmole) of (III) and 1.56 g (13 mmole) of pivaloyl chloride in 5 ml of methylene chloride. The mixture was stirred for 20 min and decomposed with a mixture of ice and sodium carbonate. After the usual treatment and removal of the solvents we obtained 2.35 g of a residue, from which by recrystallization from a 10:1 mixture of hexane and benzene we isolated 0.66 g (24%) of 1-methyl-2-phenyl-3-pivaloylcyclohexanol (XVII); mp 160°C (sublimation). Found %: C 78.73; H 9.85. $C_{18}H_{26}O_2$. Calculated %: C 78.86; H 9.60. IR spectrum (ν, cm^{-1}): 3592 (OH), 1702 (C=O). PMR spectrum: 0.92 s [9H, $C(CH_3)_3$]; 1.17 s (3H, CH_3); 1.62 (OH); 3.07 d (1H, CHPh, J_{aa} = 11.4 Hz); 3.43 td (1H, CHCO, J_{aa} = 11.4, J_{ae} = 3.5 Hz); 7.18 s (5H, C_6H_5). Mass spectrum, m/e: 274 $(M)^+$, 256 $(M - H_2O)^+$, 217 $(M - C_4H_9)^+$, 199 $(M - C_4H_9 - H_2O)^+$, 171 $(M - COC_4H_9 - H_2O)^+$. The mother solution after isolation of (XVII) was evaporated and distilled under vacuum. The first fraction [0.35 g (20%), bp 80-86°C (1 mm Hg)] took the form of a mixture of at least four hydrocarbons. According to GLC (Reoplex-400, 180°C), it contained 10-15% of the initial compound (III), and according to the mass spectrum it contained $C_{13}H_{18}$ hydrocarbons (m/e 174). Found %: C 88.98; H 10.02. $C_{13}H_{18}$. Calculated %: C 89.57; H 10.43. The second fraction [0.38 g (15%), bp 96-99°C (1 mm Hg)] was 1-methyl-2-phenyl-3-pivaloylcyclohexene (XIX). IR spectrum (ν, cm^{-1}): 1700 (C=O), 1665 w (C=C), 1600 (C_6H_5). PMR spectrum: 0.75 s [9H, $C(CH_3)_3$]; 1.47 s (3H, CH_3); 3.84 m (1H, CHCO); 6.8-7.3 m (5H, C_6H_5). From the residue after distillation, by preparative TLC (aluminum oxide, 1:1:1 benzene−hexane−ether), we isolated 0.16 g (6%) of 2-methyl-1-phenyl-3-pivaloylcyclohexanol (XVIII); R_f ~ 0.3. Found %: C 78.96; H 9.57.

$C_{18}H_{26}O_2$. Calculated %: C 78.86; H 9.60. IR spectrum (ν, cm^{-1}): 3609 w, 3384 (OH), 1690, 1700 (C=O, intramolecular hydrogen bond). PMR spectrum: 0.61 d (3H, CH_3, $J \approx 7$ Hz); 1.13 s [9H, $C(CH_3)_3$]; 3.15 q (1H, CHCO, $J_{ae} \approx J_{ee} \approx 5$ Hz); 4.30 s (1H, OH); 7.05-7.55 m (5H, C_6H_5).

A 0.35-g yield (20%) of a colorless glassy hydrocarbon was also isolated; $R_f \sim 0.95$. Found %: C 89.23; H 9.46. $(C_{13}H_{16})_n$. Calculated %: C 90.58; H 9.42.

Alternative Synthesis of (XVIII). From equimolar amounts of the trans-diketone (XIIa) and phenylmagnesium bromide in ether we obtained 35% of the hydroxy ketone (XVIII) and 60% of the isomeric 2-methyl-1-phenyl-3-pivaloylcyclohexanol; mp 129-130°C. IR spectrum (ν, cm^{-1}): 3600 (OH), 1708 (C=O).

Dehydration of the Hydroxy Ketone (XVII). To a solution of 0.27 g (1 mmole) of (XVII) in 3 ml of $C_2H_4Cl_2$ we added five drops of trifluoroacetic acid and 0.1 g of phosphorus pentoxide. After 15 min the mixture was washed with water and dried with sodium sulfate. After distillation of the solvent 0.26 g of a viscous liquid containing about 90% of (XIX) (GLC, SE-30, 190°C) was obtained.

CONCLUSIONS

The decomposition of the complex obtained in the reaction of pivaloyl tetrafluoroborate with norcarane and its 1-methyl and 1-phenyl derivatives by water gives 1-hydroxy-3-pivaloyl derivatives of cyclohexanes and the corresponding unsaturated ketones. The hydride decomposition of the same complex leads to derivatives of 6-oxabicyclo[3.2.1]octane.

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