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REACTIONS OF ALKALI METAL ANIONS. XV. REACTION OF KETONES WITH ALKALI METAL ANIONS*

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Abstract: The potassium anions were found to react with ketones to yield both alcoholates and enolates. On the basis of the ESR and ^{39}K NMR measurements the mechanism of this reaction is proposed. According to the proposed mechanism in the first step a ketyl radical is formed which after disproportionation yields an enolate and an alcoholate but only in the case of ketones having hydrogen atom in α-position in respect to carbonyl group.

Introduction:

The blue alkali metals solutions in ethers are known to contain cations and anions of metal and also solvated electrons[1]. Solutions with high metal concentration have been obtained using cation complexing compounds such as cryptands[1-4], crown ethers[1,3,5] or poly(ethylene oxide)[6]. The method producing alkali metal solutions abounded in metal ions containing only negligible amount of electrons has been recently reported[5].

In spite of detailed studies of alkali metal solution, their application in chemical synthesis is still limited. The sodium and potassium solutions have been used for reduction of alkins and aromatic hydrocarbons[7] and as initiators in anionic polymerization[4,8]. Reactions of γ- and β-lactones with potassium anions associated with crowned potassium cations lead to lactone enolization and to unexpected C–C bond cleavage, respectively, as described by us recently[9,10]. In the present paper we report on the reaction of cyclanones with potassium anions. The influence of the ring size on the outcome of this reaction is also discussed.

Results:

Potassium solution abounded in metal anions associated by complexed potassium cations produced as described previously[5] was reacted with some ketones such as cyclobutanone, cyclopentanone, cyclohexanone, acetone and benzophenone.

The proposed reaction pathway is given in the Scheme 1 and Scheme 5 respectively.

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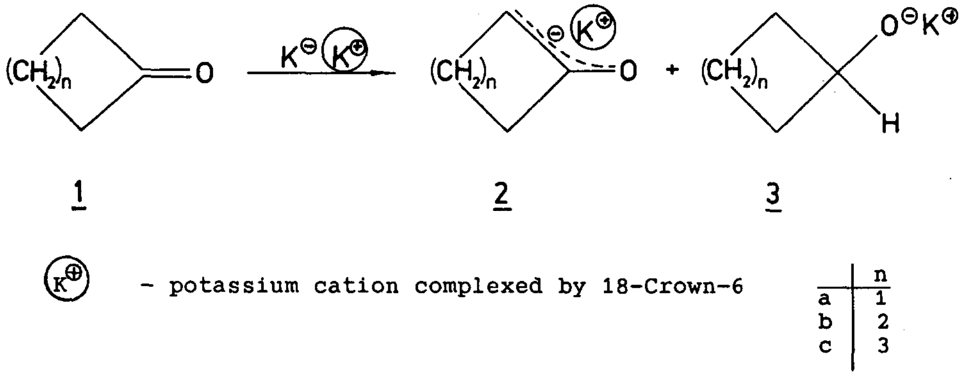
* Previous papers from this series-see references 9 and 10.



Scheme 1

The resulting products: enolate anions 2, respective alcoholates 3 and a small amounts of aldol condensation products were isolated and analyzed. Yields of the respective products of the reaction are given in the Table 1

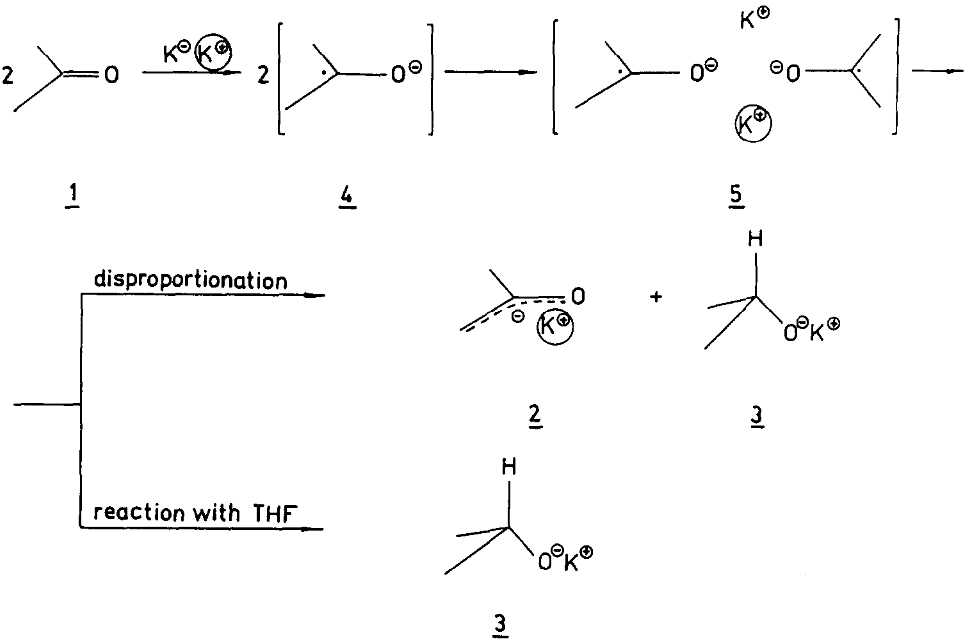
Table 1
Results of cyclanones reaction with potassium anions*.

Substrate	Products Yields %		
/\ $_n(H_2C)$ C=O \/	Reaction Scheme 1		Reaction Scheme 2
	Cyclanol	Cyclanone	Condensation Product
n = 1	70	20	<2
n = 2	37	57	6
n = 3	43	48	8

*) See details of reagents compositions in Experimental Section.

It turned out that the outcome of this reaction was different as could be expected. According to literature date[11,12] the ketone reaction with strong bases yields enolates but reduction products are not observed. On the other hand the well explored[13,14] reduction of cyclanones with metal hydrides is consider to proceed via nucleophilic substitution at the carbonyl double bond. However in the reaction of cyclic ketones with potassium anions we have found both the enolization and the reduction to proceed simultaneously. The potassium hydride formation being not observed in contrary to previous suggestions.

According to obtained experimental results the following reaction course may be proposed (Scheme 2).



Scheme 2

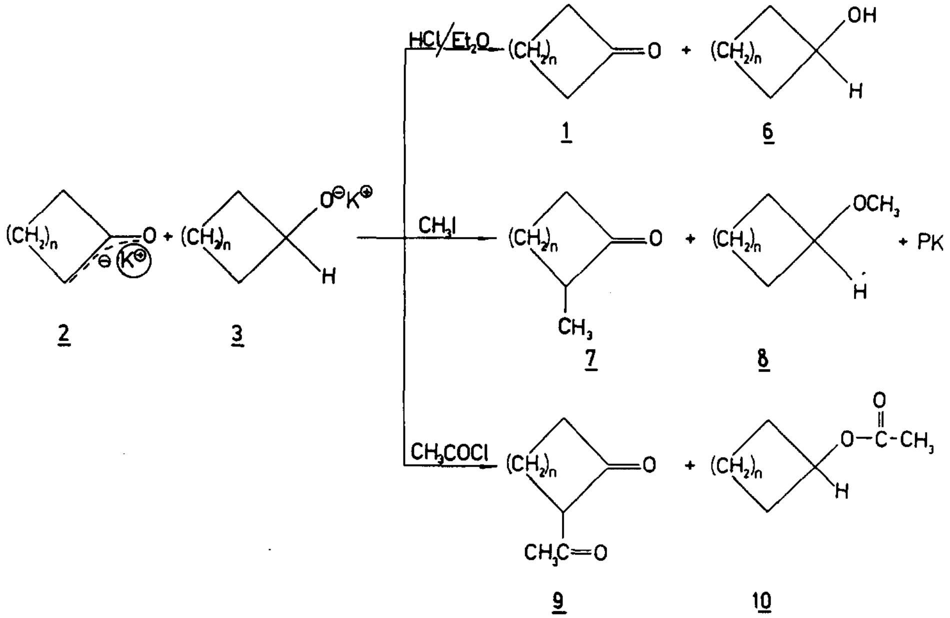
According to the above scheme a single electron is transferred from potassium anion to each ketone molecule 1, to produce at the first stage ketyl radicals 4 forming ketyl ion quadruplets 5. The lack of pinacolines in reaction products leads to the conclusion that the ketyl radicals 4 do not dimerize. In the next stage the possible quadruplets 5 disproportionate forming appropriate ketone enolate anion and alcoholate.

A side reaction with THF involving proton abstraction and yielding the appropriate alcoholate is also possible. Similar reactions of radicals, radical anions and enolate anions with aprotic solvents such as ethyl ether and THF in the presence of a complexing agent have been described in the literature[15,16,17].

The reaction of cyclic ketones depends on the ring size. The high yield of reduction of cyclobutanone (up to 70%) is due to the strong tendency to strain release of 4-membered ring. The additional source of hydrogen atoms origins from the reaction of a ketyl radical with the solvent. The yields of alcohols in the reactions of cyclopentanone, cyclohexanone and acetone are up to 50 %.

Alkyl and acyl derivatives of cyclanones can be easily produced from enolate anions as can be seen in Scheme 3.

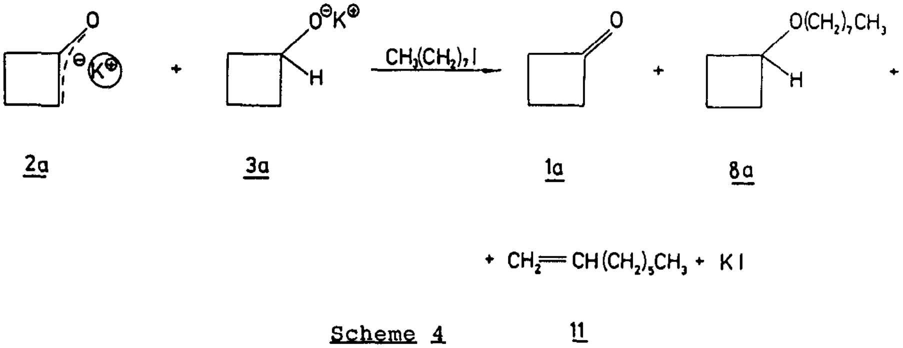
In the alkylation and acylation reactions carried out in described conditions O-alkylation or O-acylation of enolate are not observed.



where:PK = polyalkylated ketones (small yields)

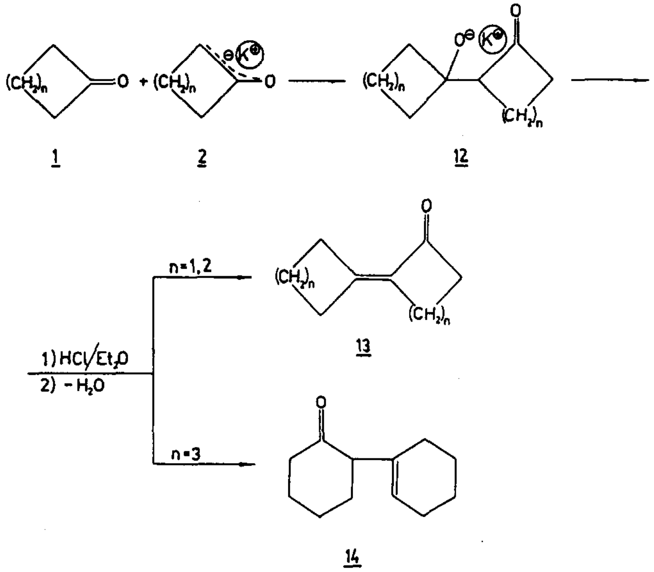
Scheme 3

In the reactions with higher alkyl halides however the β-elimination occurs producing alkene derivatives in reasonable yields (Scheme 4).



Scheme 4

It turned out that the enolates formed are able not only to nucleophilic substitution with alkyl halides but can react with cyclanones to yield dimers and their respective isomers (Scheme 5). This side reaction of the aldol-type condensation is accelerated by the fast addition of a given ketone to the reaction mixture so it can be somewhat kept under control.



Scheme 5

Discussion of ESR measurements:

The ESR spectra of potassium solutions in THF containing 18-crown-6 display only an intense singlet (Fig. 1a), which corresponds to the small amounts of solvated electron (e_s^-) present also in the origin metal solution abounded in potassium anions. The distinct signal of solvated electron vanishes after the addition of a ketone having hydrogen atom in α-position, e.g. acetone or cyclanone.

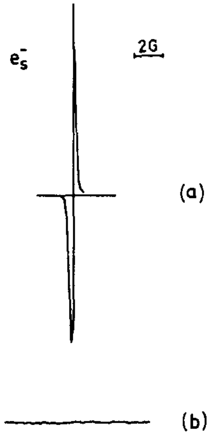


Fig. 1

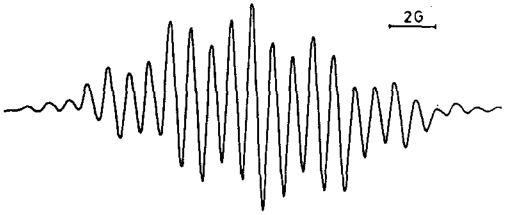


Fig. 2

The lack of ESR signal after the addition of acetone or cyclanone is due to very quick disproportionation reaction of ketyl radicals, (see Scheme 2). Similar results have been obtained by Rautenstrauch[16,18] for ketones having hydrogen atoms in α-position in the case of the reaction of alkali metal solutions in liquid ammonia. On the other hand in the case of 2,2,6,6-tetramethylcyclohexanone in an aprotic solvent the characteristic ESR signal of the ketyl radical due to the lack of disproportionation reaction has been observed[19]. Similar picture was observed in our experiment after addition of benzophenone instead of a cyclanone to the metal solution. After the reaction of benzophenone with metal solution the signal of the solvated electron disappeared and a broad splitted multiplet consisting of 25 lines due to benzophenone anion radical (benzophenone ketyl) in ESR spectrum was however observed (Fig.2). The determined splitting constants $a_o^H=0.252$, $a_m^H=0.082$ $a_p^H=0.35$ and relative line intensities are in good agreement with literature data concerned with benzophenone anion radical[20]. The benzophenone ketyl radical signal in ESR spectrum is due to the lack of hydrogen atom in α-position making the disproportionation reaction impossible.

Discussion of ^{39}K NMR measurements:

The ^{39}K NMR spectra of potassium solutions in THF containing 18-crown-6 exhibit two signals. The very broad signal which corresponds to the potassium cation complexed by 18-crown-6 and the intense singlet can be assigned to potassium anion[21] (Fig. 3a).

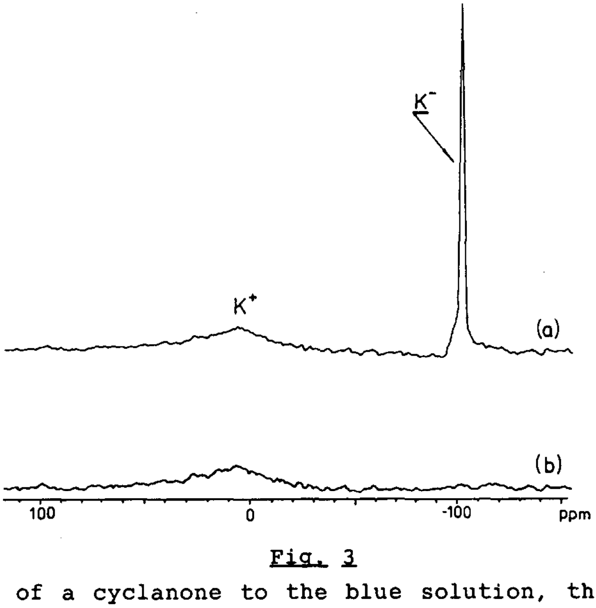


Fig. 3

After addition of a cyclanone to the blue solution, the intense singlet disappeared completely, but no essential changes of complexed cation signal are observed (Fig. 3b). This result indicates that the potassium anions react with ketones via electron transfer from metal anions to ketone molecules.

Conclusions:

The results of experiments indicate that the reaction course of ketones reaction with potassium anions associated with crowned cations is different from that described for the reactions of ketones with strong bases, as well as that with metal hydrides. The single electron transfer takes place from a potassium anion to a ketone molecule with formation of a ketyl radical. The anion radicals form quadruplets which next disproportionate yielding enolates and alcoholates. Products of anion radicals dimerization were not observed.

The composition of reaction mixture depends on the kind of a ketone employed. The high strain in small ring cyclanones accelerates the reduction and increases the yield of produced alcoholates due to the side reactions with THF.

Ketones having no hydrogen atoms in α-position e.g. benzophenone however do not undergo disproportionation and the obtained anion radical is stable and corresponding signal in ESR spectrum can be observed.

It is also interesting to note that the course of the reaction of 4-membered cyclobutanone with potassium anion involving singlet electron transfer is quite different from previously described reaction of potassium anion with a respective lactones e.i. 4-membered β-lactones[10].

Experimental Section

Boiling temperatures were not corrected. Gas chromatographic analyses were performed using Varian 2800 gas chromatograph equipped with a preparative unit. GC analyses were carried out on a glass column packed with OV-17, 15% on Chromosorb W DMSC, 80-100 mesh. Preparative separations were run on a column packed with OV-17, 20% on Chromosorb W DMSC, 45-60 mesh. Compounds were identified by their IR, UV, ^{1}HNMR and mass spectra. IR spectra were taken on a Specord M80 instrument, UV spectra were determined with a Specord UV-VIS spectrophotometer. ^{1}HNMR spectra were taken in $CDCl_3$ solution on a Varian VXL-300 instrument using TMS as internal standard. GC-MS data were obtained on a Varian MAT 711 mass spectrometer at 70eV, with ion source temperature of 200°C, and independently on Finnigan MAT 800 AT mass spectrometer.

ESR measurements. Electron Spin Resonance observations were performed on a SE/X-2542 spectrometer (ZAR "Radiopan") with a rectangular cavity operating at a microwave frequency of ca. 9.5 GHz. Spectra were recorded as first derivatives. The alkali metal solutions and reagents concentrations were of 0.1 mol/L.

^{39}K NMR measurements. ^{39}K NMR measurements were carried out on a Varian VXR-300 multinuclear spectrometer operating at ^{39}K resonance frequency of

14 MHz and ^{1}H resonance frequency of 300 MHz. Spectra were recorded at 253 K with 85 μs $\pi/2$ ^{39}K pulse width and 0.2 s delay between pulse sequence repetitions.

Materials

Cyclobutanone **1a** (Aldrich) was dried over molecular sieves 4A and distilled in an atmosphere of dry argon. The fraction boiling at 99°C was collected (99,8%GC). Cyclopentanone **1b** (Aldrich) was dried over molecular sieves 4A and distilled in an atmosphere of dry argon. The fraction boiling at 130,5°C was collected (99,7%GC). Cyclohexanone **1c** (POCh) was dried over molecular sieves 4A and distilled in an atmosphere of dry argon. The fraction boiling at 155,5°C was collected (99,8% GC). Acetone (POCh) was dried over molecular sieves 4A and distilled in an atmosphere of dry argon. The fraction boiling at 56.5°C was collected (99,7%GC). Benzophenone (Aldrich) was dried in the diethyl ether solution over molecular sieves 4A. Then the diethyl ether was evaporated and benzophenone was distilled in an atmosphere of dry argon. The fraction boiling at 224°C (100 mmHg) was collected (99.8% GC). Methyl iodide (Aldrich) was dried over calcium chloride and distilled in an atmosphere of dry argon. The fraction boiling at 42°C was collected (99.6% GC). Octyl iodide (Aldrich) was dried over calcium chloride and distilled in an atmosphere of dry argon. The fraction boiling at 86°C (5mm Hg) was collected (99.8 % GC). Acetyl chloride (Aldrich) was purified by distillation in an atmosphere of dry argon. The fraction boiling at 51-52°C was collected (99,8%GC). HCL solution in diethyl ether (2,6mol/L) was obtained by saturation of dry diethyl ether (FLUKA), purified and dried as described[22a], with dry gas hydrochloride.18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (FLUKA) was purified by precipitation of its complex with acetonitrile. Acetonitrile was then removed under high vacuum and the crown ether was dried under vacuum at the temperature 50°C during 48h. THF (tetrahydrofuran) (POCh) was purified according to ref.[22b] and then was dried over a sodium -potassium alloy in an atmosphere of dry argon.

Reaction of Potassium Solutions with Ketones

Preparation of the potassium solutions and reaction of potassium anions with ketones were performed in the apparatus depicted in ref.[10]. The potassium solution was obtained by a contact of potassium mirror with a solution of 18-crown-6 in THF (0,2mol/L) at -20°C. After exactly 15 min the resulting blue solution was filtered through a coarse frit to the reactor and equimolar amount of ketone (solution in THF 1 mol/L) was added dropwise until the discoloration of potassium solution ($[K^-]$=0,2 mol/L).

The reaction mixture was subsequently protonated or alkylated and acylated by corresponding alkyl or acyl halides.

Protonation. Protonation of reaction mixture obtained from potassium solution and ketone 1c. Into the reaction mixture obtained from 590mg (6mmol) of ketone 1c and 15 ml potassium solution the 2.35 ml HCl solution in Et_2O (2,6 mol/L) was introduced under the argon atmosphere. The reaction was conducted during 30 min at room temperature. The potassium chloride formed was filtered. Then the reaction mixture was washed with saturated aqueous solution of NaCl (three times, 10ml), and dried over anhydrous $MgSO_4$. The crude products were evaporated under reduced pressure together with THF and then the final products were isolated by distillation using Hickman apparatus or by preparative gas chromatography. The following products were obtained:

Cyclohexanone, (1c): yield, 285mg (48%), b.p.156°C; MS, m/e 98 (M^+); IR (neat), ν=2940, 2864, 1712, 1448, 1312, 1220, 1120 ,1052, 1016, 992, cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.74 (m,2H), 1.88 (quint,4H), 2.34 (t,4H).

Cyclohexanol, (6c):yield, 258mg (43%), b.p. 161°C; MS, m/e 100(M^+); IR (neat),ν=3390, 2940, 2856, 1448, 1364, 1296, 1256, 1064, 1024, 972 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.26, 1.55 (m,m,6H), 1.73, 1.90 (m,m,4H) 2.37 (s,1H,), 3.61 (m,1H).

2-Cyclohexenylcyclohexan-1-one, (14):yield, 43mg (8%), b.p. 113°C (2mm Hg); MS, m/e 178 (M^+); IR (neat), ν=3404, 3040, 2920, 2860, 1708, 1620, 1450, 1336, 1312, 1196, 1124, 1064, 1024, 920, 828, 800 cm^{-1}; UV (95% EtOH) 209nm (ϵ 1300); ^{1}HNMR ($CDCl_3$),δ=1.53-1.79 (m,6H), 1.82-1.95 (m,4H), 1.96-2.07(m,4H), 2.31-2.44 (m,2H), 2.89 (m,1H), 5.43 (m,1H).

Protonation of reaction mixture obtained from potassium solution and ketone 1b, 505mg (6mmol). The reaction was conducted as described above and the following products were obtained:

Cyclopentanone, (1b): yield, 285mg (57%), b.p. 130°C; MS, m/e 84 (M^+); IR (neat), ν=2968, 2884, 1745, 1456, 1408, 1268, 1152, 960, 836 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.97 (m,4H), 2.17 (t,4H)

Cyclopentanol, (6b): yield, 190mg (37%), b.p. 141°C; MS, m/e 86 (M^+); IR (neat), ν=3356, 2968, 2872, 1452, 1340, 1176, 1076, 996, 840 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.56 (m,4H), 1.77 (m,4H), 2.30 (s,1H), 4.33(m,1H)

2-Cyclopentylidenecyclopentanone, (13b): yield, 25mg (6%), b.p.251-252°C; MS, m/e 150 (M^+); IR (neat), ν=2960, 2872, 1708, 1640, 1452, 1416, 1252, 1172 cm^{-1}; UV (95% EtOH) 259nm (ϵ 10800); ^{1}HNMR ($CDCl_3$), δ=1.70(m,4H), 1.92 (m.4H), 2.32 (t,2H), 2.54 (m,2H), 2.78 (m,2H).

Protonation of reaction mixture obtained from potassium solution and ketone 1a, 420 mg (6mmol). The reaction was conducted as described above and the following products were obtained:

Cyclobutanone, (1a): yield, 85 mg (20%), b.p. 100°C; IR (neat), ν=3005, 2972, 2932, 1796, 1392, 1208, 1080, 730 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=2.02 (m,2H), 3.10 (t,4H).

Cyclobutanol, (6a): yield, 300 mg (70%), b.p. 125°C; IR (neat), ν=3400, 2940, 2870, 1448, 1340, 1236, 1128, 960, 752 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.43, 1.64 (m,m,2H), 1.89, 2.27 (m,m,4H), 2.98 (s,1H), 4.22 (m,1H).

2-Cyclobutylidenecyclobutanone, (13a) : yield < 2%, identified only by UV spectrum[23]; UV (95% EtOH) 253 nm (ϵ=13400)

Protonation of reaction mixture obtained from potassium solution and acetone, 350 mg (6mmol). The reaction was conducted as described above and the following products were obtained:

Acetone: yield, 150mg (43%), b.p. 56°C; MS, m/e 58(M^+); IR (neat),ν=3004,2968, 2924, 1712, 1420, 1364, 1220, 1092, 904, 788 cm^{-1}; UV (95% EtOH) 272nm(ϵ 12); ^{1}HNMR ($CDCl_3$), δ=2.14 (s,6H).

2-Propanol: yield, 170mg (47%), b.p. 82°C; MS, m/e 60(M^+); IR (neat),ν=3348,2980, 2936, 2896, 1468, 1404, 1380, 1340, 1308, 1160, 1132, 952, 816 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.17 (d,6H), 3.00 (s,1H), 3.95 (m,1H).

Alkylation. Methylation of reaction mixture obtained from potassium solution and ketone 1c. Into the reaction mixture obtained from 590mg (6mmol) of ketone 1c and 15 ml potassium solution the 0.86g (6 mmol) methyl iodide was added under the argon atmosphere. The reaction was conducted during 60 min at room temperature. The potassium iodide formed was filtered. Then the reaction mixture was washed with saturated aqueous solution of NaCl (three times, 10ml) and dried over anhydrous $MgSO_4$. The crude products were evaporated under reduced pressure together with THF and then the final products were isolated by distillation using Hickman apparatus or by preparative gas chromatography. The following products were obtained:

2-Methylcyclohexanone, (7c): yield, 269mg (40%), b.p. 165°C; MS, m/e 112 (M^+); IR (neat), ν=2965, 2932, 2864, 1712, 1448, 1376, 1312, 1216, 1124, 1052, 988 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.03 (d,3H), 1.38, 1.86 (m,m,2H), 1.67 (m,2H), 2.08 (m,2H), 2.37 (m,3H).

Cyclohexyl methyl ether, (8c): yield, 254mg (37%), b.p. 135°C; MS, m/e 114 (M^+); IR (neat), ν=2944, 2856, 2820, 1452, 1368, 1204, 1180, 1152,1104, 1020, 936 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ= 1.26, 1.54 (m,m,6H), 1.73 (m,2H), 1.92 (m,2H), 3.14 (m,1H), 3.34 (s,3H).

Methylation of reaction mixture obtained from potassium solution and ketone 1b, 505 mg (6 mmol). The reaction was conducted as described above and the following products were obtained:

2-Methylcyclopentanone, (7b): yield, 270mg (46%), b.p. 140°C; IR (neat), ν= 2964, 2876, 1736, 1460, 1408, 1372, 1272, 1156, 1044, 1008, 928, 816 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.09 (d,3H), 1.34, 1.65 (m,m,2H), 1.85 (m,1H), 1.96 (m,2H), 2.11 (m,2H).

Cyclopentyl methyl ether, (8b): yield, 192mg (32%), b.p. 106°C; IR (neat), ν= 2972, 2916, 2820, 1452, 1364, 1212, 1152, 1100, 968, 928, 900, 824 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.53, 1.68 (m,m,8H), 3.28 (s,3H), 3.80 (m,1H).

Alkylation of reaction mixture obtained from potassium solution and ketone 1a, 420 mg (6mmol) by octyl iodide. The reaction was conducted as described above and the following products were isolated by preparative gas chromatography:

Cyclobutanone, (1a): yield, 25% GC; analytical data were identical with that of protonation reaction.

Cyclobutyl octyl ether, (8a): yield, 55% GC; IR (neat), ν= 2960, 2928, 2856, 1732, 1468, 1340, 1240, 1152, 1120 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=0.88 (t,3H), 1.28 (m,12H), 1.54, 1.62 (m,m,2H), 1.89, 2.17 (m,m4H), 3.31 (t,2H), 3.89 (m,1H).

1-Octene, (11): yield, 60% GC; IR (neat), ν= 2960, 2928, 2860, 1708, 1645, 1462, 1380, 1175 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=0.89 (t,3H), 1.29 (m,8H), 2.04 (m,2H), 4.96 (m,2H), 5.82 (m,1H).

Acylation. Acylation of reaction mixture obtained from potassium solution and ketone 1c. Into the reaction mixture obtained from 590mg (6 mmol) of ketone 1c and 15 ml potassium solution the 0.47g (6 mmol) acetyl chloride was added under the argon atmosphere. The reaction was conducted during 30 min at room temperature. The potassium chloride formed was filtered. Then the reaction mixture was washed with saturated aqueous solution of $NaHCO_3$ and afterwards with saturated aqueous solution of NaCl (three times,10ml), and dried over anhydrous $MgSO_4$. The crude products were evaporated under reduced pressure together with THF, and then the final products were isolated by distillation using Hickman apparatus or by preparative gas chromatography. The following products were obtained:

2-Acetylcyclohexanone, (9c): yield, 350mg (42%), b.p. 96°C (10mmHg); IR (neat), ν=2940, 2864, 1724, 1700, 1620, 1416, 1364, 1312, 1240, 1176, 1020, 956 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ= 1.69 (m,4H), 2.13 (s,3H), 2.33 (m,5H).

Cyclohexyl acetate, (10c): yield, 320mg (37%), b.p. 175°C; IR (neat), ν=2940, 2860, 1728, 1452, 1376, 1364, 1264, 1124, 1048, 1020, 968, 908

cm^{-1}; ^{1}HNMR ($CDCl_3$), δ=1.38, 1.55 (m,m,6H), 1.73, 1.86 (m,m,4H), 2.03 (s,3H), 4.74 (m,1H).

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