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Ionic Hydrogenation of α,β-Unsaturated Ketones with Cyclohexane in the Presence of Aluminum Halides*, **

K. Yu. Koltunov, I. B. Repinskaya, and G. I. Borodkin

Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia
e-mail: organic@fen.nsu.ru

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Abstract—4-Methyl-3-penten-2-one, 3-hepten-2-one, 3-methyl-1-phenyl-2-buten-1-one, 4-(2,4-dichlorophenyl)-, 4-(4-hydroxyphenyl)-, 4-(4-methoxyphenyl)-, 4-(2-hydroxyphenyl)-, and 4-(4-dimethylaminophenyl)-3-buten-2-ones, and 3-(4-methoxyphenyl)-1-phenyl-2-propenone react with cyclohexane in the presence of excess aluminum chloride or aluminum bromide in CH_2Cl_2 or CH_2Br_2, respectively, at room temperature to form the corresponding saturated ketones in high yields. Using 4-phenyl- and 4-(4-methoxyphenyl)-3-buten-2-ones as examples, it was shown that the reaction pattern does not change in going from the Lewis acids $AlCl_3$ and $AlBr_3$ to proton-donor acid system $CF_3SO_3H–SbF_5$. The reactive intermediates are likely to be C-protonated complexes of α,β-unsaturated ketones with aluminum halides or their O,C-diprotonated analogs.

In continuation of our studies on acid-catalyzed reactions of unsaturated compounds with weak nucleophiles we turned our attention to the reaction of α,β-unsaturated ketones with alkanes. With 4-methyl-3-penten-2-one (**Ia**) as an example we previously demonstrated the possibility for hydride reduction of enones with alkanes in the presence of Lewis acids [1]. The reaction occurred under mild conditions and resulted in formation of 4-methylpentan-2-one in a good yield. Caustard *et al.* [2] reported on the reduction with methylcyclopentane of a double bond conjugated with a carbonyl group in some steroid compounds in the superacid system $HF–SbF_5$. The goal of the present work was to examine the reaction of α,β-unsaturated ketones with alkanes in the presence of aluminum halides. We studied the effect of the reaction conditions, substrate structure, and nature of the medium; the structure of the reactive intermediate was also considered.

The reactions of α,β-unsaturated ketones were carried out with excess cyclohexane and Lewis acid (aluminum chloride or bromide), using methylene chloride or bromide as solvent (depending on the aluminum halide taken). In all cases the reactions occurred at room temperature (Scheme 1).

4-Methyl-3-penten-2-one (**Ia**), 3-hepten-2-one (**Ib**), and 3-methyl-1-phenyl-2-buten-1-one (**Ic**) were smoothly reduced to 4-methyl-2-pentanone (**IIa**), 2-heptanone (**IIb**), and 3-methyl-1-phenyl-1-butanone (**IIc**) in 65, 70, and 95% yield, respectively (Table 1). It is seen that replacement of the methyl group in the carbonyl moiety of enone **Ia** by phenyl (**Ic**) has no appreciable effect on the reactivity. However, comparison of the reaction conditions for compound **Ib**, on the one hand, and enones **Ia** and **Ic**, on the other, shows an appreciable effect on their reactivity of the structure of the olefin fragment.

The main pathway of the above reactions is hydride ion transfer from cyclohexane to the substrate, which leads to hydrogenation of the double carbon–carbon bond. The presence of a phenyl group in the olefin moiety gives rise to a number of side processes. In the reaction of 4-phenyl-3-buten-2-one (**Id**) with cyclohexane in the presence of aluminum chloride (reaction time 1 h) we obtained a complex mixture of products. According to the GC–MS data, this mixture contained 4-phenyl-2-butanone (**IId**), products of its mono- and dialkylation with C_6-cations, ketones **III** and **IV** (which were formed as a result of elimination of hydride ion from cyclohexane), and 4,4′-*p*-phenylenebis(2-butanone) (**V**). The ratio **IId** : **III** : **IV** : **V** was 2.3 : 1 : 2.3 : 6.3. Ketone **V** was isolated from the mix-

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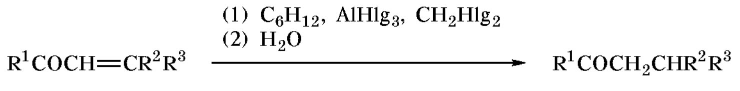
Scheme 1.

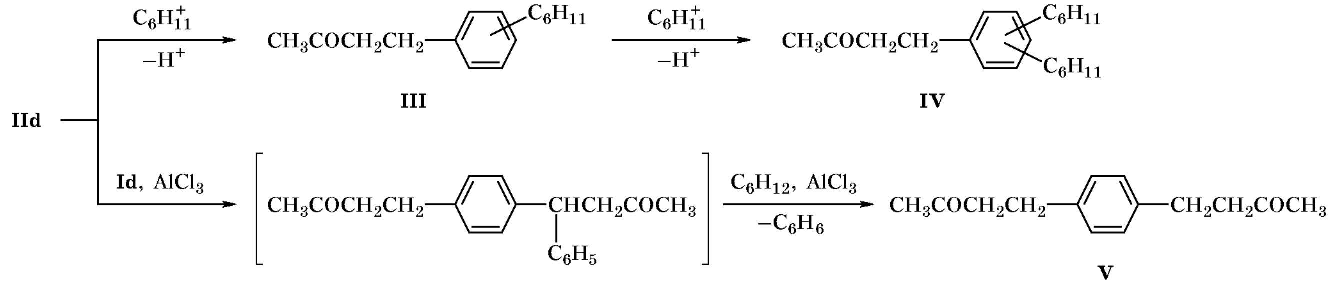


$$R^1COCH{=}CR^2R^3 \xrightarrow[(2)\ H_2O]{(1)\ C_6H_{12},\ AlHlg_3,\ CH_2Hlg_2} R^1COCH_2CHR^2R^3$$

Ia–Ij **IIa–IIj**

I, **II**, $R^1 = R^2 = R^3 = CH_3$ (**a**); $R^1 = CH_3$, $R^2 = H$, $R^3 = C_3H_7$ (**b**); $R^1 = C_6H_5$, $R^2 = R^3 = CH_3$ (**c**); $R^1 = CH_3$, $R^2 = H$, $R^3 = C_6H_5$ (**d**); $R^1 = CH_3$, $R^2 = H$, $R^3 = 2,4\text{-}Cl_2C_6H_3$ (**e**); $R^1 = CH_3$, $R^2 = H$, $R^3 = 4\text{-}HOC_6H_4$ (**f**); $R^1 = CH_3$, $R^2 = H$, $R^3 = 4\text{-}CH_3OC_6H_4$ (**g**); $R^1 = CH_3$, $R^2 = H$, $R^3 = 2\text{-}HOC_6H_4$ (**h**); $R^1 = C_6H_5$, $R^2 = H$, $R^3 = 4\text{-}CH_3OC_6H_4$ (**i**); $R^1 = CH_3$, $R^2 = H$, $R^3 = 4\text{-}(CH_3)_2NC_6H_4$ (**j**).

Scheme 2.



ture in the pure form. Presumably, it was formed by reaction of ketone **IId** with enone **Id** [4] and subsequent elimination of phenyl group from the condensation product [5] and further hydrogentation of the elimination product (Scheme 2).

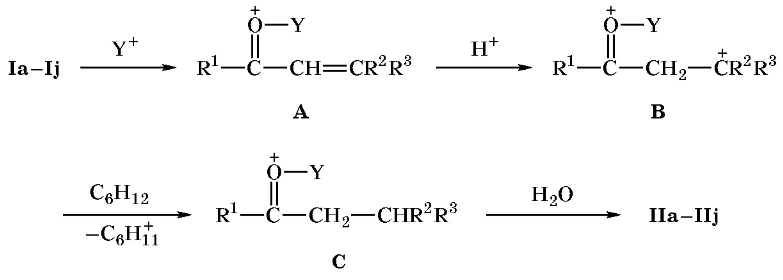
It was reasonable to expect that introduction into the phenyl group of the olefinic moiety of enone of an electron-acceptor substituent or a substituent capable of being converted into electron-acceptor one via complex formation with aluminum halide (OR, NR_2, etc.) should hamper undesirable alkylation of the aromatic ring. The results of our experiments were in full agreement with the above expectations. 4-(2,4-Dichlorophenyl)-3-buten-2-one (**Ie**) was smoothly reduced with cyclohexane in the presence of excess aluminum chloride, yielding 87% of 4-(2,4-dichlorophenyl)-2-butanone. Enones having phenyl groups with substituents which can be modified via complex formation behaved similarly. 4-(4-Hydroxyphenyl)-3-buten-2-one (**If**), 4-(4-methoxyphenyl)-3-buten-2-one (**Ig**), 4-(2-hydroxyphenyl)-3-buten-2-one (**Ih**), and 3-(4-methoxyphenyl)-1-phenyl-2-propenone

Table 1. Reduction of α,β-unsaturated ketones **Ia**–**Ij** with cyclohexanone in the presence of aluminum halides at room temperature

Initial compound	Product	Acid system	Reaction time, h	Yield, %
Ia	**IIa**	$AlCl_3$, CH_2Cl_2	1	65[a]
Ib	**IIb**	$AlBr_3$, CH_2Br_2	40	70[b]
Ic	**IIc**	$AlCl_3$, CH_2Cl_2	3	95
Id	**IId**	$AlCl_3$, CH_2Cl_2	1	18[c]
Ie	**IIe**	$AlCl_3$, CH_2Cl_2	30	87
If	**IIf**	$AlCl_3$, CH_2Cl_2	15	95
Ig	**IIg**	$AlCl_3$, CH_2Cl_2	3	90
Ih	**IIh**	$AlBr_3$, CH_2Br_2	3	60[d]
Ii	**IIi**	$AlCl_3$, CH_2Cl_2	3	95
Ij	**IIj**	$AlBr_3$, CH_2Br_2	135	97

[a] With pentane as reducing agent the reaction time was 48 h; yield 64%; conversion 78%.
[b] In the presence of $AlCl_3$ (CH_2Cl_2) the reaction time was 102 h; conversion 25% (according to the NMR data).
[c] A complex mixture of products was obtained (see text).
[d] The reaction in the presence of $AlCl_3$ was accompanied by intramolecular cyclization of the substrate [3].

Scheme 3.



Y = H, $Al_mHlg_{3m}^-$.

(**Ii**) were thus reduced to 4-(4-hydroxyphenyl)-2-butanone (**IIf**), 4-(4-methoxyphenyl)-2-butanone (**IIg**), 4-(2-hydroxyphenyl)-2-butanone (**IIh**), and 3-(4-methoxyphenyl)-1-phenyl-1-propanone (**IIi**) in 95, 90, 60, and 95% yield, respectively. The complete reduction of 4-(4-dimethylaminophenyl)-3-buten-2-one (**Ij**) in the presence of aluminum bromide required keeping of the reaction mixture for a long time (135 h), and the yield of 4-(4-dimethylaminophenyl)-2-butanone (**IIj**) was almost quantitative (Table 1).

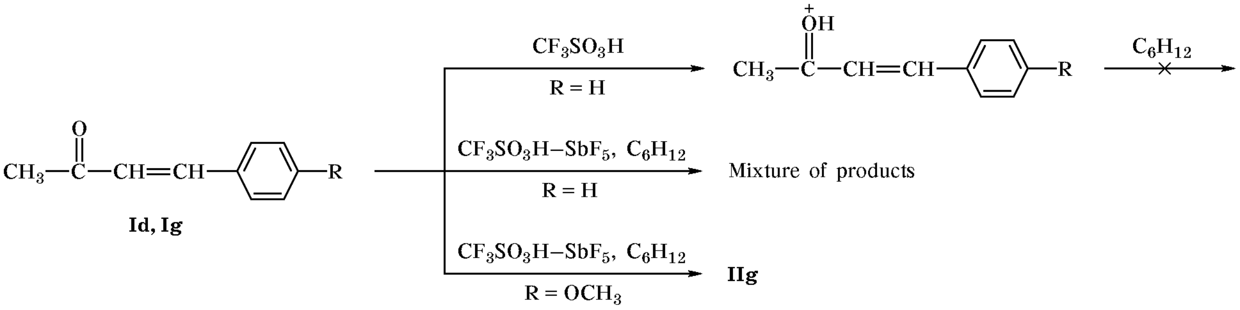
The use of a cyclic alkane for reduction of α,β-unsaturated ketones is not necessary. The reaction can also be effected with an acyclic alkane. For example, enone **Ia** was reduced with pentane in the presence of aluminum chloride at room temperature. After 48 h, the yield of ketone **IIa** was 64%, the conversion of enone **Ia** being 78%.

Apart from saturated ketones, the reaction mixtures in all cases contained isomeric hydrocarbons of the general formula $C_{12}H_{22}$. These products were formed by reaction of C_6-cations with C_6H_{12} cycloalkanes (cyclohexane in acid medium exists as an equilibrium mixture with methylcyclopentane, and cyclohexyl cation, with methylcyclopentyl cations [6, 7]). In the reaction mixture obtained from compound **Id** and cyclohexane we detected (by GC–MS) 11 $C_{12}H_{22}$ isomers. In none of the cases products of reduction of the carbonyl group to hydroxy were found (cf. [8]).

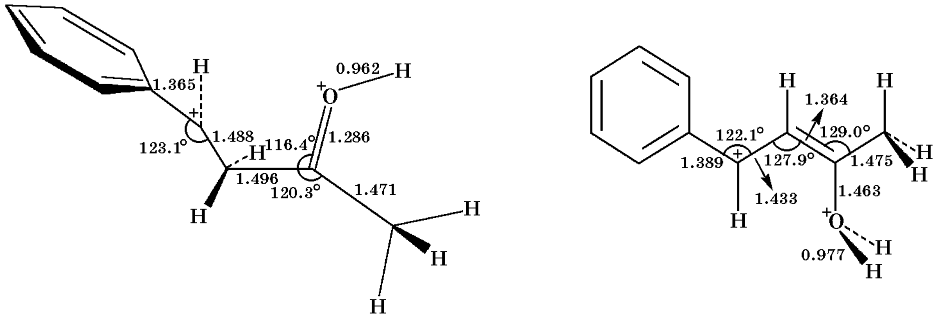
Our results indicate that aluminum halides effectively catalyze ionic hydrogenation of the double carbon–carbon bond in α,β-unsaturated ketones, except for the substrates containing in the olefinic moiety an unsubstituted phenyl ring or a phenyl ring having donor substituents. The high catalytic activity of aluminum halides makes it possible to perform the process at room temperature, attaining complete transformation of the substrate. Taking into account that alkanes are among the most accessible organic raw materials, the reaction under study seems to be promising from the practical viewpoint as a convenient method of reduction of the double C=C bond in enones, which is more advantageous than the other methods [9].

Another important aspect of the present study is the way of transformation of α,β-unsaturated ketone into a superelectrophilic species capable of abstracting hydride ion from alkane. Like saturated ketones, enones could readily give complexes of type **A** with aluminum halides (Scheme 3, Y = $Al_mHlg_{3m}^-$) [10, 11]. Such complexes are structurally related to O-protonated ketones **A** (Y = H) which could be formed concurrently to complex formation, taking into account

Scheme 4.



Id, R = H; **Ig**, **IIg**, R = OCH_3.



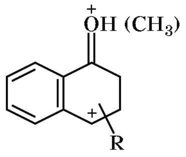
E-1 **E**-2

Structures of dications **E**-1 and **E**-2 optimized by the MNDO/PM3 method. The bond lengths are given in Å.

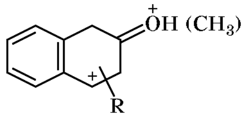
the presence in the reaction mixture of trace amounts of a strong protic acid and the low basicity of enones (pK_{BH^+} ranges from –5 to –7 [12]).

However, the electrophilicity of carboxonium ions, and probably of the enone complexes, is insufficient to abstract hydride ion from alkanes [8, 11]. The same also follows from the results of our experiments with enone **Id** and cyclohexane in strong protic acids. According to the ^{1}H NMR data, enone **Id** in CF_3SO_3H (H_0 = –14.1 [7]) at 25°C undergoes complete protonation at the oxygen atom to give ion **VI** of type **A** ($R^1 = C_6H_5$, $R^2 = R^3 = CH_3$, Y = H), which does not react with cyclohexane for at least 5 h. Addition of SbF_5 to a CF_3SO_3H–SbF_5 molar ratio of 1 : 1 leads to disappearance of signals belonging to ion **VI** in 10 min. After appropriate treatment, the reaction mixture was identical to that obtained previously in the reaction of **Id** with cyclohexane in the presence of aluminum chloride (see Experimental). Likewise, enone **Ig** in the acid system CF_3SO_3H–SbF_5 (molar ratio 2 : 1) at 25°C quickly reacted with cyclohexane, affording ketone **IIg** in quantitative yield (Scheme 4).

Thus, superacidic medium (H_0 < –14.1) is required for ionic hydrogenation of α,β-unsaturated ketones, indicating that a stronger electrophile than carboxonium ion is necessary. We believe that in the presence of a protic acid such a superelectrophile may be O,C-diprotonated enone **B** (Y = H, Scheme 3). The possibility for formation of such cationic species was demonstrated by us previously using low-temperature ^{1}H and ^{13}C NMR spectroscopy with enones **Ia** and **Id** as examples in the acid system HF–SbF_5–SO_2FCl. Therefore, O,C-diprotonated forms of α,β-unsaturated ketones were postulated as reactive intermediates in the reactions with arenes [13]. Structurally related dicationic species were observed previously for 1- and 2-naphthol derivatives and the corresponding methyl ethers (structures **VII** and **VIII**) in media with enhanced acidity [14]. They were assumed to be intermediates in reactions of naphthols and naphthyl ethers with nonactivated arenes and alkanes [15, 16].



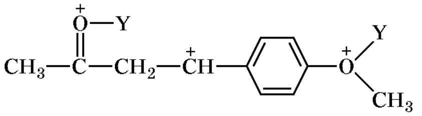
VII



VIII

Probably, aluminum halides give rise mainly to a similar kind of activation, namely complex formation between aluminum halide and enone and subsequent C-protonation of the complex, leading to structurally analogous intermediate dicationic species **B** (Y = $Al_mHlg^-_{3m}$, Scheme 3). In both cases, superelectrophilic intermediate **B** abstracts hydride ion from alkane, yielding cation **C**. The latter is converted into ketone **II** on treatment of the reaction mixture with water.

Enones **If**–**Ij** containing OH, OCH_3, and $N(CH_3)_2$ groups in the benzene ring could be activated additionally via protonation or complex formation of Lewis acid at the above groups, which should enhance the electrophilicity of ions thus formed. For example, in the reduction of enone **Ig** the superelectrophilic intermediate may be C-protonated form coordinated to aluminum halide through both oxygen atoms or analogous tricationic species **D**.



$$CH_3{-}\overset{\overset{+}{O}-Y}{\overset{\|}{C}}{-}CH_2{-}\overset{+}{C}H{-}C_6H_4{-}\overset{+}{O}(Y)CH_3$$

D

Ohwada *et al.* [16] proposed an alternative path of superelectrophilic activation of α,β-unsaturated

Table 2. Calculated (MNDO/PM3) heats of formation (ΔH_f), charges on atoms, and energies of the frontier molecular orbitals of dications **E**-1 and **E**-2

Dication	ΔH_f, kcal/mol	ε_{HOMO}, eV	ε_{LUMO}, eV	q_1	q_2	q_3	q_4	q_O
E-1	430.7	–17.93	–10.44	–0.226	0.434	–0.183	0.154	–0.085
E-2	458.5	–17.78	–10.64	–0.133	0.023	–0.080	0.093	0.043

enones in reactions with another weak nucleophile, benzene, in the acid system $CF_3SO_3H–SbF_5$ [16]. The reactive intermediates were assumed to be dications formed by addition of two protons to the enone oxygen atom [16]. However, the formation of such species was not confirmed experimentally [11, 16]. Probably, the dications are present in acid medium at a very low equilibrium concentration or fast exchange with the medium occurs. The participation of O,O-diprotonated forms of enones in reactions with weak nucleophiles can be substantiated on the assumption that they are stronger electrophiles than the corresponding O,C-diprotonated species. To verify this assumption we performed MNDO/PM3 quantum-chemical calculations [17] of the dications derived from enone **Id** via protonation of the O and C atoms (structure **E**-1) and double protonation of the oxygen atom (**E**-2). The calculation results are presented in Table 2, and figure shows the optimized geometries of dications **E**-1 and **E**-2 (some bond lengths and bond angles are also given). Unlike dication **E**-1, the carbon and oxygen atoms in structure **E**-2 lie in one plane. Dication **E**-1 is more stable than **E**-2 by 28 kcal/mol. The energies of the lowest unoccupied molecular orbitals (ε_{LUMO}) are fairly similar. Taking into account the higher stability of dication **E**-1 and the greater positive charge on C^4 therein, its formation as reactive intermediate is more probable than the formation of **E**-2.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 spectrometer at 250.13 MHz for ^1H and 62.9 MHz for ^{13}C. The chemical shifts were measured relative to the solvent signals ($CDCl_3$, δ 7.28 ppm and δ_C 76.9 ppm). The chemical shifts of cationic species in acid solutions were measured relative to tetramethylammonium tetrafluoroborate (δ 3.2 ppm). Gas chromatographic–mass spectrometric analysis* was performed using a Hewlett–Packard G 1081-A system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector; energy of ionizing electrons 70 eV; HP-5 column, 30 m × 0.25 mm × 0.25 μm, 5% of biphenyl and 95% of dimethylsiloxane; carrier gas helium, 1 ml/min; oven temperature programming from 50°C (2 min) at a rate of 10°C/min to 280°C (5 min); injector temperature 280°C; ion source temperature 173°C. Quantum-chemical calculations were performed by the MNDO/PM3 procedure [17] with full geometry optimization using HyperChem 5.02 software. The progress of reactions was monitored by TLC on Silufol UV-254 plates; spots were visualized with iodine vapor or under UV light; eluent hexane–ethyl acetate, 5 : 1. Ketones **IIb**, **IIc**, **IIe**, **IIi**, and **IIj** were isolated by column chromatography on silica gel using hexane–ethyl acetate, 10 : 1. Aluminum bromide of analytical grade and aluminum chloride and trifluoromethanesulfonic acid from Merck were used. Cyclohexane of chemically pure grade and reagent-grade methylene chloride and methylene bromide were distilled prior to use. Antimony pentafluoride was distilled under atmospheric pressure in a stream of argon. Enone **Ia** was synthesized by self-condensation of acetone; enones **Ib**, **Id**, **Ie**, **Ig**, **Ih**, and **Ij** were prepared by condensation of acetone with butanal, benzaldehyde, 2,4-dichlorobenzaldehyde, 4-methoxybenzaldehyde, 2-hydroxybenzaldehyde, and 4-(dimethylamino)benzaldehyde, respectively, in the presence of a 10% solution of NaOH [18]. Enone **Ii** was synthesized in a similar way by condensation of acetophenone with 4-methoxybenzaldehyde. Compound **If** was obtained by demethylation of **Ig** (a mixture of **Ig** and aluminum bromide at a molar ratio of 1 : 3 in CH_2Br_2 was kept for 5 h at room temperature [19]). Enone **Ic** was synthesized by bromination of 1-phenyl-3-methyl-1-butanone with bromine and subsequent dehydrobromination with 1,8-diazabicyclo[5.4.0]undec-7-ene [18].

4-Methyl-2-pentanone (IIa). *a.* A suspension of 15 g (0.15 mol) of enone **Ia**, 27 g (0.2 mol) of aluminum chloride, and 15 g (0.17 mol) of cyclohexane in 40 ml of CH_2Cl_2 was stirred for 1 h at room temperature. The mixture was poured onto ice, the

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* The authors are grateful to L.M. Pokrovskii for carrying out the GC–MS analysis.

products were extracted into ether, and the extract was washed with water and dried over $MgSO_4$. By distillation we isolated 10 g (65%) of ketone **IIa**; the ^{1}H NMR spectral parameters of the product coincided with those reported in [20].

b. An analogous experiment was carried out with the same amounts of enone **Ia** and aluminum chloride and 37 g (0.35 mol) of pentane. The mixture was stirred for 48 h at room temperature and was then treated as described above and analyzed by GLC. The conversion of enone **Ia** was 78%, and the yield of ketone **IIa** was 64% on the reacted enone.

2-Heptanone (IIb). A solution of 0.5 g (4 mmol) of enone **Ib**, 3 g (10 mmol) of aluminum bromide, and 2 g (20 mmol) of cyclohexane in 5 ml of CH_2Br_2 was kept for 40 h at room temperature. The mixture was poured onto ice, and the organic layer was washed with a solution of sodium carbonate and water, and dried over $MgSO_4$. The organic solution was carefully evaporated, and the residue was subjected to chromatography. We isolated 0.36 g (70%) of ketone **IIb**. The ^{1}H NMR spectrum of the product coincided with that reported in [20].

3-Methyl-1-phenyl-1-butanone (IIc). A suspension of 1 g (0.006 mol) of enone **Ic**, 2 g (0.015 mol) of aluminum chloride, and 3 g (0.035 mol) of cyclohexane in 15 ml of CH_2Cl_2 was stirred for 3 h at room temperature. The mixture was poured onto ice, and ketone **IIc** was isolated as described above for compound **IIb**. Yield 0.97 g (95%). The ^{1}H and ^{13}C NMR spectra of the product coincided with those of an authentic sample.

Reaction of enone Id with cyclohexane. *a.* A suspension of 1.46 g (0.01 mol) of enone **Id**, 6 g (0.045 mol) of aluminum chloride, and 5 g (0.06 mol) of cyclohexane in 25 ml of CH_2Cl_2 was stirred for 1 h at room temperature. The mixture was poured onto ice and extracted with ether. The combined extracts were dried over $MgSO_4$ and carefully evaporated, and the residue (2 g) was analyzed by GC–MS. It contained hydrocarbons of the general formula $C_{12}H_{22}$ (total of 11 isomers), ketones **IId**, **III**, **IV**, and diketone **V**; yield 18.6, 5.4, 9, and 67%, respectively. Ketone **IId** was identified by comparing its mass spectrum with that of an authentic sample; isomeric $C_{12}H_{22}$ hydrocarbons and ketones **III**–**V** were identified by analyzing their mass spectra.

Mass spectrum of one of the $C_{12}H_{22}$ isomers, *m*/*z* (I_{rel}, %): 166 (70.8) M^+, 151 (58.6), 137 (0.4), 123 (0.37), 109 (31.1), 95 (90.4), 81 (100), 67 (53.9), 55 (42.5), 41 (32.0). Mass spectrum of ketone **III**, *m*/*z* (I_{rel}, %): 230 (83.8) M^+, 172 (99.7), 157 (15.0), 143 (46.6), 131 (98.5), 117 (100), 105 (3.3), 91 (72.5), 83 (35.2) [C_6H_{11}], 55 (31.8) [CH_3COCH_2], 43 (91.5) [CH_3CO], 41 (15.3). Mass spectrum of ketone **IV**, *m*/*z* (I_{rel}, %): 312 (71.6) M^+, 187 (58.0), 171 (51.7), 161 (14.9), 143 (11.7), 141 (12.2), 129.1 (45.7), 115 (15.2), 105 (36.4), 91 (25.2), 83 (100), 55 (62.5), 43 (41.3) [CH_3CO], 41 (23.5). Mass spectrum of diketone **V**, *m*/*z* (I_{rel}, %): 218 (13.7) M^+, 175 (0.5), $[M-CH_3CO]^+$, 160 (31.5), $[M-CH_3COCH_2]^+$, 117 (100), 91 (115), 43 (59.3) [CH_3CO].

The residue (see above) was distilled under reduced pressure. A fraction with bp 124–128°C (3 mm) crystallized; it was diketone **V**, mp 47–50°C (from ethanol) [21]. ^{13}C NMR spectrum, δ_C, ppm: 29.03 ($C^{1'}$), 29.28 ($C^{3'}$), 44.67 ($C^{2'}$), 128.03 (C^2, C^3, C^5, C^6), 138.44 (C^1, C^4), 203.0 (C=O).

b. An NMR ampule was charged with 0.75 g (0.005 mol) of CF_3SO_3H, 26 mg (3 mmol) of cyclohexane, and 30 mg (2 mmol) of enone **Id**. The ^{1}H NMR spectrum of the solution showed the presence of O-protonated enone **Id**, δ, ppm: 3.02 s (3H, CH_3), 7.44 d (1H, =CHCO, J = 15.3 Hz), 7.67 t (2H, 3′-H, J = 7.77 Hz), 7.86 t (2H, 4′-H, J = 7.8 Hz), 8.03 d (2′-H, J = 7.8 Hz), 8.98 d (1H, =CHC_6H_5, J = 15.3 Hz). The spectrum did not change after keeping the acid solution for 5 h at 25°C.

To the acid solution we added 1.1 g (0.005 mol) of SbF_5, and the mixture was stirred and, 10 min after, poured onto ice. The organic phase was extracted into ether, and the solvent and volatile components were distilled off to obtain 35 mg of the residue which, according to the GC–MS data, contained $C_{12}H_{22}$ hydrocarbons, ketones **IId**, **III**, and **IV**, and diketone **V**; yield 9, 5, 2, and 84%, respectively.

4-(2,4-Dichlorophenyl)-2-butanone (IIe). A suspension of 0.3 g (0.001 mol) of enone **Ie**, 0.75 g (0.006 mol) of $AlCl_3$, and 1 g (0.012 mol) of cyclohexane in 10 ml of CH_2Cl_2 was stirred for 30 h at room temperature. It was then poured onto ice and extracted with ether, and the extract was washed with water and dried over $MgSO_4$. The solvent and C_6H_{12} alkanes were carefully distilled off, and the residue was subjected to chromatography. We isolated 0.26 g (87%) of ketone **IIe**. M^+ 216.01115 ($C_{10}H_{10}Cl_2O$). ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, CH_3), 3.62 m (4H, CH_2CH_2), 7.15 br.s (2H, 5′-H, 6′-H), 7.36 br.s (1H, 3′-H). ^{13}C NMR spectrum, δ_C, ppm: 27.03 (C^4), 29.8 (C^1), 42.77 (C^3), 127.02 ($C^{5'}$), 129.14 ($C^{6'}$), 131.34 ($C^{3'}$), 132.5 ($C^{4'}$), 134.35 ($C^{2'}$), 137.05 ($C^{1'}$), 207.03 (C=O).

4-(4-Hydroxyphenyl)-2-butanone (IIf). A suspension of 0.1 g (6 mmol) of enone **If**, 0.33 g (0.002 mol) of aluminum chloride, and 0.8 g (0.009 mol) of cyclohexane in 5 ml of CH_2Cl_2 was stirred for 15 h at room temperature. The mixture was poured onto ice, the products were extracted into ether, the extract was treated with a 10% solution of NaOH, and the alkaline solution was acidified and extracted with ether. The extract was dried and evaporated to obtain 0.1 g (95%) of ketone **IIf**, mp 81–83°C (from benzene) [3].

4-(4-Methoxyphenyl)-2-butanone (IIg). *a.* A suspension of 1 g (0.006 mol) of enone **IIg**, 3 g (0.022 mol) of $AlCl_3$, and 3 g (0.035 mol) of cyclohexane in 15 ml of CH_2Cl_2 was stirred for 3 h at room temperature. The mixture was treated as described above, volatile components were removed, and the residue was subjected to chromatographic separation to isolate 0.86 g (85%) of ketone **IIg** which was identified by ^1H NMR spectroscopy [20].

b. Enone **Ig**, 20 mg (1 mmol), was dissolved in a mixture of 0.75 g (0.005 mol) of CF_3SO_3H and 0.54 g (2.5 mmol) of SbF_5, and 20 mg (2 mmol) of cyclohexane was added to the solution. After 5 min, the mixture was poured onto ice. After appropriate treatment, we isolated 16.2 mg (80%) of ketone **IIg**.

4-(2-Hydroxyphenyl)-2-butanone (IIh). A solution of 0.5 g (0.003 mol) of enone **Ih**, 3.5 g (0.013 mol) of $AlBr_3$, and 3 g (0.035 mol) of cyclohexane in 10 ml of CH_2Br_2 was kept for 3 h at room temperature. The mixture was treated as described above for ketone **IIf** to isolate 0.3 g (60%) of product **IIh**. mp 45–46°C (from petroleum ether).

3-(4-Methoxyphenyl)-1-phenyl-1-propanone (IIi). A suspension of 1.2 g (0.005 mol) of enone **Ii**, 4 g (0.03 mol) of aluminum chloride, and 3 g (0.035 mol) of cyclohexane in 20 ml of CH_2Cl_2 was stirred for 3 h at room temperature. The mixture was treated as described above for compound **IIg** to isolate 1.15 g (95%) of ketone **IIh**. mp 63–67°C (from petroleum ether) [22].

4-(4-Dimethylaminophenyl)-2-butanone (IIj). A solution of 0.38 g (0.002 mol) of enone **Ij**, 3.5 g (0.013 mol) of aluminum bromide, and 2 g (0.02 mol) of cyclohexane in 15 ml CH_2Br_2 was stirred for 135 h at room temperature. The mixture was poured onto ice and extracted with chloroform, and the extract was washed with water and dried over $MgSO_4$. Volatile components were removed, and the residue was subjected to chromatography to isolate 0.37 g (97%) of ketone **IIj**. mp 48–51°C (from aqueous ethanol) [23].

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