A new efficient and selective synthesis of ketones from alkanes or cycloalkanes, CO, and silanes in the presence of aprotic superacids

I. S. Akhrem, I. M. Churilova, A. V. Orlinkov, L. V. Afanas'eva, S. V. Vitt, and P. V. Petrovskii*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: cmoc@ineos.ac.ru

A new approach to the direct synthesis of ketones from alkanes or cycloalkanes (RH), CO, and silanes is proposed. Ketones were obtained in 50—97% yields from propane, butane, cyclopentane, cyclohexane, and methylcyclopentane on treatment with CO and silanes (Me_4Si, Et_4Si, or *m*- and *p*-$XC_6H_4SiMe_3$, where X = Cl, Me, OMe) in the presence of $CX_4 \cdot 2AlBr_3$ (X = Br, Cl) superacids at 0 °C. The reactions with *m*- and *p*-$XC_6H_4SiMe_3$ (X = Cl, Me) occur regioselectively to give *m*-ketones from *m*-silanes and *p*-ketones from *p*-silanes. However, the only product, *p*-$MeOC_6H_4COR$, is formed both from *m*- and *p*-$MeOC_6H_4SiMe_3$. The reaction of *cyclo*-$C_5H_9CO^+$ with $BzSiMe_3$ results in an organosilicon ketone, $Me_3SiCH_2C_6H_4COC_5H_9$, while in the presence of an excess of an acylating system (after alcoholysis), $Me_2Si(OR')CH_2C_6H_4COR$ is formed.

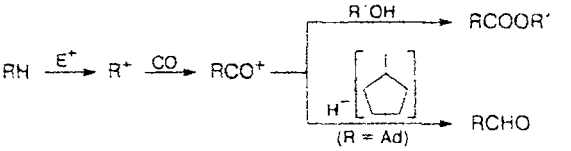
Key words: alkanes, cycloalkanes, functionalization with CO and silanes; organosilanes; carbon monoxide; acyldesilylation; polyhalomethanes, complexes with aluminum halides; aprotic superacids.

Selective synthesis of organic compounds directly from accessible alkanes and cycloalkanes is one of the most important problems of organic chemistry. Although significant success has been achieved in alkane chemistry over the last 20—25 years,[1—4] examples of direct functionalization of alkanes and cycloalkanes are rather infrequent. In addition, nonselectivity is a drawback of the majority of alkane reactions whose initiation requires hard systems. In the present work, we suggest a new simple and efficient approach to the synthesis of ketones from alkanes or cycloalkanes, CO, and organosilanes.

Previously,[5—11] we found that polyhalomethanes combined with aluminum halides behave as extremely strong aprotic organic superacids, which efficiently initiate various transformations of *n*-alkanes and cycloalkanes, including their selective functionalization.

Results and Discussion

Reactions of alkanes[7] and cycloalkanes[8,9] with CO occur according to the Koch—Haaf mechanism[12] involving carbocation generation from a saturated hydrocarbon followed by addition of CO and formation of an acylium cation. Alkyl carboxylates[7—9] and an aldehyde (in the case of adamantane, AdH)[10] have been obtained in high yields and with high selectivity using acylium cation trapping agents (an alcohol or methylcyclopentane).



Using a similar approach, we attempted to utilize silanes as donors of alkyl and aryl groups for the initially formed acylium cations. This approach made it possible to synthesize ketones from alkanes and cycloalkanes. The reactions occur in high yields (50—97% with respect to the electrophile (E)) and with high selectivity, and in some cases regioselectively.

$$RH \xrightarrow{E^+} R^+ \xrightarrow[(a)]{CO} RCO^+ \xrightarrow[(b)]{R'SiR''_3} RCOR'$$

RH = PrH, Bu^nH, *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, *cyclo*-C_5H_9Me; E = $CCl_4 \cdot 2AlBr_3$; $CBr_4 \cdot 2AlBr_3$; R' = Me, Et, *m*-MeC_6H_4, *p*-MeC_6H_4, *m*-ClC_6H_4, *p*-ClC_6H_4, *m*-$MeOC_6H_4$, *p*-$MeOC_6H_4$; $R'SiR''_3$ = Me_4Si, Et_4Si, *m*-$XC_6H_4SiMe_3$, *p*-$XC_6H_4SiMe_3$ (X = Cl, Me, OMe)

The reactions of alkanes and cycloalkanes with CO were carried out at atmospheric pressure at temperatures from −20 to 0 °C in CH_2Br_2 for 1 h (step *a*). After adding a silane, the reaction was continued in a CO atmosphere for 15—30 min at the same temperature (step *b*). The structures of the ketones obtained were

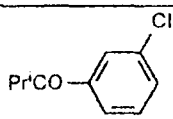
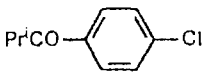
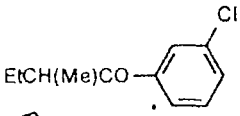
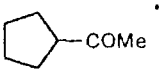
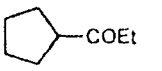
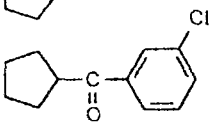
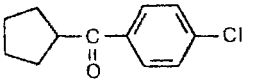
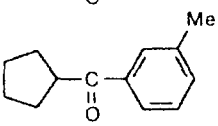
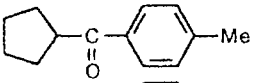
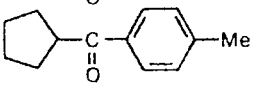
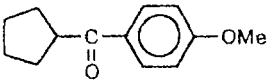
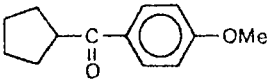
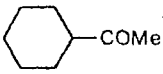
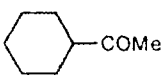
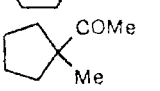
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 947—952, May, 1998.

1066-5285/98/4705-0918 $20.00

confirmed by their mass spectra. The positions of substituents at the aromatic ring were determined from ^1H NMR spectra.

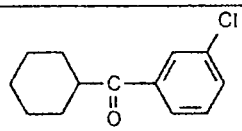
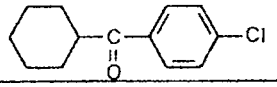
Ketones of the cyclopentyl series, *cyclo*-C_5H_9COR', are formed from cyclopentane (Table 1). The reactions starting from cyclohexane or from methylcyclopentane

Table 1. Direct synthesis of ketones from alkanes (cycloalkanes), CO, and silanes or aromatic hydrocarbons[a] on treatment with $CCl_4 \cdot 2AlBr_3$ (E) in CH_2Br_2 at 0 °C

RH	Silane	Ketone	
		Structure	Yield (mol.% with respect to E)
Pr^nH	*m*-$ClC_6H_4SiMe_3$		72
Pr^nH	*p*-$ClC_6H_4SiMe_3$		97
Bu^nH[b]	*m*-$ClC_6H_4SiMe_3$		50
cyclo-C_5H_{10}	Me_4Si		97
cyclo-C_5H_{10}	Et_4Si		68
cyclo-C_5H_{10}	*m*-$ClC_6H_4SiMe_3$		81
cyclo-C_5H_{10}	*p*-$ClC_6H_4SiMe_3$		98
cyclo-C_5H_{10}	*m*-$MeC_6H_4SiMe_3$		65
cyclo-C_5H_{10}	*p*-$MeC_6H_4SiMe_3$		66
cyclo-C_5H_{10}	PhMe		92
cyclo-C_5H_{10}	*m*-$MeOC_6H_4SiMe_3$		60
cyclo-C_5H_{10}	PhOMe		81
cyclo-C_6H_{12}	Me_4Si		87
cyclo-C_6H_{12}	Me_4Si[c]		30
			52

(to be continued)

Table 1 (*continued*)

RH	Silane	Ketone	
		Structure	Yield (mol.% with respect to E)
cyclo-C_6H_{12}	*m*-$ClC_6H_4SiMe_3$		59
cyclo-C_6H_{12}	*p*-$ClC_6H_4SiMe_3$		69

[a] A silane was added to the reaction mixture containing an acylium cation obtained from a hydrocarbon and CO in CH_2Br_2 at 0 °C in 1 h, and the reaction was continued for 15—30 min. Treatment with an alcohol or water gave a ketone.
[b] Carbonylation was carried out at −20 °C in the presence of $CBr_4 \cdot 2AlBr_3$, and the subsequent reaction with a silane was carried out at 0 °C for 30 min.
[c] Carbonylation was carried out at −40 °C for 1 h, and the subsequent reaction with Me_4Si was carried out at −20 °C for 30 min.

afford either pure ketone *cyclo*-$C_6H_{11}COR'$ (**1**) or a mixture of compound **1** and *cyclo*-1,1-MeC_5H_8COR' (**2**) in a ratio depending on the reaction temperature. In order to obtain pure ketone **2**, the carbonylation of cyclohexane was carried out at −40 °C, *i.e.*, under the conditions of the formation of *cyclo*-1,1-$MeC_5H_8CO^+$,[9] but transfer of the methyl group from Me_4Si was not observed at this temperature. The reaction of 1,1-$MeC_5H_8CO^+$ (synthesized from cyclohexane and CO, −40 °C, 1 h) with Me_4Si at −20 °C for 0.5 h gives a mixture of two isomeric ketones **1** and **2** in 1.0 : 1.6 ratio. At 0 °C, both cycloalkanes give rise only to ketone **1**. The reaction starting from propane gives exclusively the Pr^{i}COR′ ketones (see Table 1).

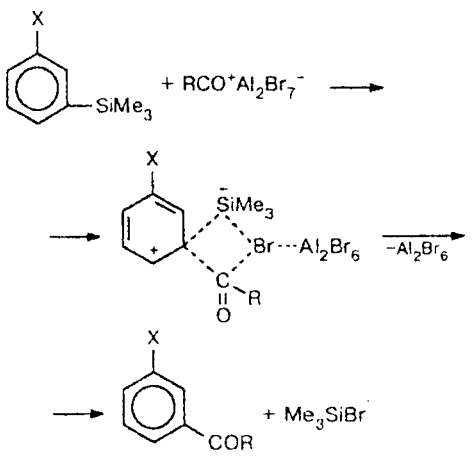
We recently found that carbonylation of butane on treatment with CO in the presence of $CBr_4 \cdot 2AlBr_3$ or $CCl_4 \cdot 2AlBr_3$ in CH_2Br_2 at −20 to 0 °C for 1 h followed by hydrolysis (or alcoholysis) gives pivalic acid (or its ester) as the main product (in 80% yield). The yield of an isomeric product EtCH(Me)COOH (or its ester) is no higher than 20%.[13] In view of this, it was surprising that the reaction of $BuCO^+$ with *m*-$ClC_6H_4SiMe_3$ gives *m*-$ClC_6H_4COCH(Me)Et$ instead of the expected *m*-$ClC_6H_4COCMe_3$ (see Table 1).

We demonstrated that the use of activated arenes (toluene or anisole) as trapping agents for acylium cation *cyclo*-$C_5H_9CO^+$ generated *in situ* makes it possible to obtain individual *p*-substituted ketones C_5H_9COAr (where Ar = C_6H_4Me, C_6H_4OMe) in high yields.

It should be noted that the use of silanes for the synthesis of aromatic ketones has a number of advantages in comparison with the use of arenes. First, passivated arenes (chlorobenzene), unlike activated ones (toluene, anisole), are not acylated under the reaction conditions. For example, *cyclo*-$C_5H_9CO^+$ virtually does not react with C_6H_5Cl at 0 °C in CH_2Br_2; at 20 °C, the conversion of chlorobenzene increases markedly, but diarylmethanes $ClC_6H_4CH_2C_6H_4Cl$ and products of their cycloalkylation, $ClC_6H_4CH_2C_6H_3(Cl)R$ (R = C_5H_9, C_5H_7), are formed instead of carbonyl-containing aromatic compounds. On the contrary, *m*- and *p*-$ClC_6H_4SiMe_3$ give the corresponding ketones at 0 °C in 15 min in 81—98% yields (see Table 1).

The second important advantage of using silanes (both those with activating and passivating groups) is the regioselectivity of the synthesis of aromatic ketones. For example, it was found that if substituent X cannot coordinate with an electrophile (X = Me, Cl), reactions starting from the *m*-$XC_6H_4SiMe_3$ silanes give the *m*-XC_6H_4COR ketones, while those starting from *p*-$XC_6H_4SiMe_3$ afford the *p*-XC_6H_4COR ketones, correspondingly. The regioselectivity of these reactions indicates that the reaction of RCO^+ with aromatic silanes probably occurs by the acyldesilylation involving *ipso*-attack (Scheme 1).

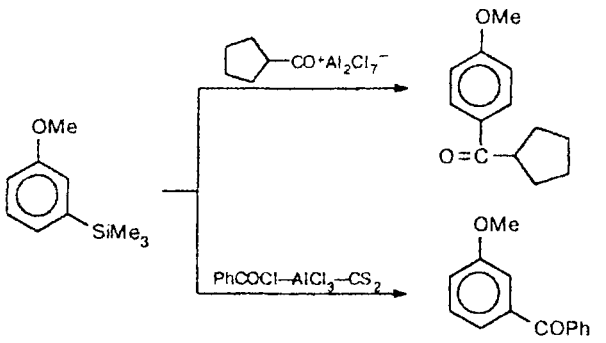
Scheme 1



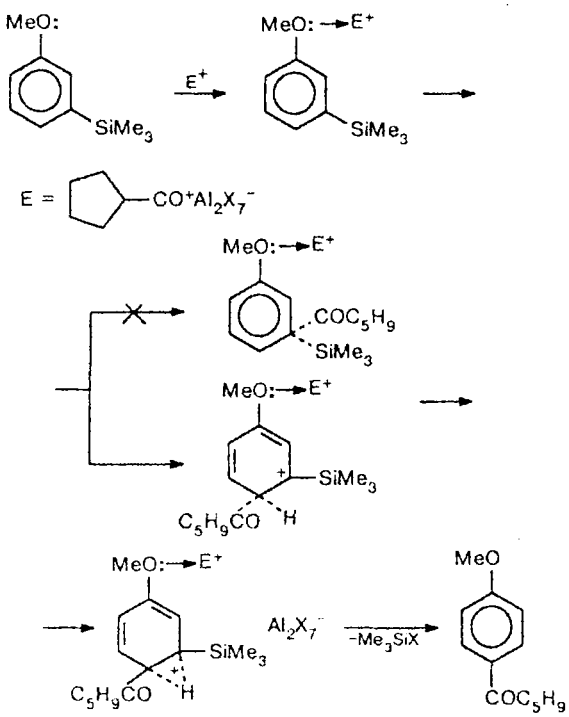
The acyldesilylation of substituted trimethylphenylsilanes on treatment with $RCOCl \cdot AlCl_3$ has been reported previously.[14,15] The particular feature of the suggested method for the synthesis of ketones is the use of acylium salts prepared *in situ* from alkanes (cycloalkanes) and CO in the presence of aprotic superelectrophiles. Although reactions of activated arenes (toluene, anisole) with RCO^+ occur readily and in high yields, only *para*-isomers can be obtained this way.

There are two facts deserving special comment. First, the reaction of *m*-$MeOC_6H_4SiMe_3$ with *cyclo*-$C_5H_9CO^+$ gives *p*-$MeOC_6H_4COC_5H_9$ (which is identical to that obtained from anisole and *cyclo*-$C_5H_9CO^+$) instead of the expected *meta*-ketone. This result is quite unexpected, especially considering that regioselective acyldesilylation of *m*-$MeOC_6H_4SiMe_3$ on treatment with the $PhCOCl—AlCl_3—CS_2$ system is known (Scheme 2).[15]

Scheme 2



Scheme 3

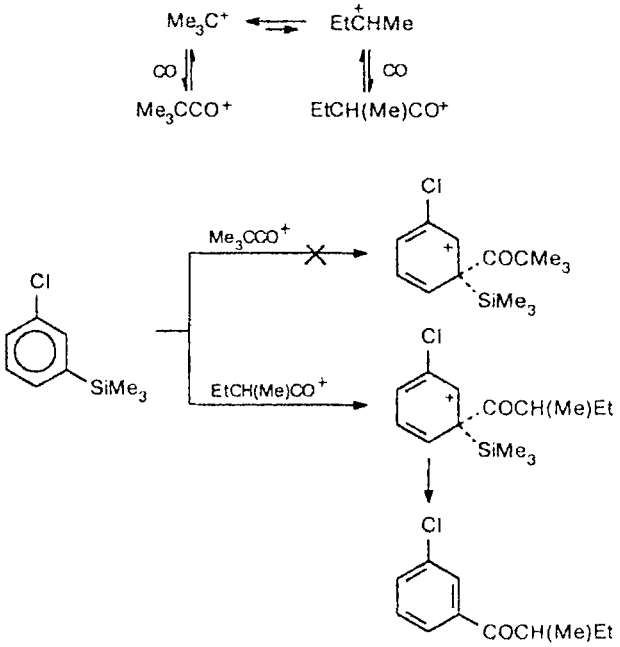


It is possible that the reason of the formation of *para*-isomers in the reaction with $C_5H_9CO^+$ is the initial coordination of the methoxy group with the bulky superelectrophilic complex, which creates considerable steric hindrance against the subsequent *ipso*-attack of the *meta*-position by the bulky electrophile. Probably, because of this the acylium cation attacks the silane at the *para*-position, and the trimethylsilyl group in the Wheland complex formed is intramolecularly replaced by a proton (Scheme 3). The fact that acyldesilylation does not occur when $C_5H_9CO^+$ is present in tenfold excess with respect to *m*-$MeOC_6H_4SiMe_3$ is consistent with the above assumption and decreases the probability of the alternative scheme involving protolytic cleavage of the initially formed ketone, $C_5H_9COC_6H_3(OMe)SiMe_3$.

In the reaction of $C_5H_9CO^+$ with *p*-$MeOC_6H_4SiMe_3$, complexation at the methoxy group does not hinder acyldesilylation.

The second unusual fact mentioned above is the formation of the *m*-$ClC_6H_4COCH(Me)Et$ ketone instead of the expected *m*-$ClC_6H_4COCMe_3$ product in the reaction of butane, CO, and *m*-$ClC_6H_4SiMe_3$. This result can be explained by the assumption that due to steric factors, acyldesilylation occurs only with the less bulky cation, $Et(Me)CHCO^+$. The reaction of the latter with the silane shifts the equilibrium towards $Et(Me)CHCO^+$ (Scheme 4).

Scheme 4



The effect of steric hindrance is probably also responsible for the absence of *ortho*-isomers among the products of reactions of acylium salts with arenes.

The reaction of Me_3SiCH_2Ph with $C_5H_9CO^+$ occurs by acylation of the starting silane to give an organosilicon

ketone, $Me_3SiCH_2C_6H_4COC_5H_9$, in quantitative yield. When an excess of *cyclo*-$C_5H_9CO^+$ with respect to benzylsilane is used, one of the Si—Me bonds of this organosilicon ketone is cleaved, and alcoholysis with R′OH gives ketones $Me_2Si(OR')CH_2C_6H_4COR$ (R′ = Et, Pr^i) in 40—50% yields.

$$Me_3SiCH_2Ph + C_5H_9CO^+ \longrightarrow Me_3SiCH_2C_6H_4COC_5H_9 \longrightarrow$$

$$\xrightarrow{C_5H_9CO^+Al_2X_7^-} Me_2Si(X)CH_2C_6H_4COC_5H_9 \xrightarrow{R'OH}$$

$$\longrightarrow Me_2Si(OR')CH_2C_6H_4COC_5H_9$$

In addition to the examples mentioned above,[14,15] it was also reported[16] that refluxing of a mixture of $RCOCl \cdot AlCl_3$ (R = Alk, Ar) with Me_4Si, Et_4Si in CH_2Cl_2 for 18 h results in the formation of RCOR′ ketones in 30—80% yields.

The new, simple, and selective, and in some cases regioselective, method for the preparation of ketones from alkanes and cycloalkanes developed in this work can be recommended for organic synthesis.

Experimental

The reaction mixtures were analyzed by gas chromatography (GC) on a Finnigan 9001 chromatograph with a flame ionization detector (DB-5.625 quartz capillary column, 30 m×0.3 mm column, helium as the carrier gas) in a linear temperature programming mode. GLC-MS analysis was performed using a similar capillary column. Mass spectra were recorded on an AEI MS 1073 instrument (ionization energy 70 eV). ^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 MHz) in CD_2Cl_2 using $SiMe_4$ as the internal standard.

Reaction with propane (general procedure). A mixture of anhydrous $AlBr_3$ (0.56 g, 2.1 mmol) and CBr_4 (0.35 g, 1.0 mmol) was placed in a two-necked round-bottomed flask (50 mL) equipped with a magnetic stirrer, and CH_2Br_2 (1 mL) was added with stirring. The homogeneous solution that formed was cooled to 0 °C, and the flask was filled with a gas mixture containing propane and CO in 1.0 : 1.3 ratio. The contents of the flask were stirred for 1 h at 0 °C under a small excess pressure of the gas mixture, then *m*-$ClC_6H_4SiMe_3$ (0.16 g, 0.86 mmol) was added, and the mixture was stirred for 0.5 h. Pr^{i}OH (3 mL) was added after that. After another 15 min, the reaction mixture was treated with water (20 mL). The organic products were extracted with CH_2Br_2, and the extracts were dried with $MgSO_4$ and analyzed by GC using benzophenone as the internal standard. According to GC data, 0.113 g (0.62 mmol) of *m*-$ClC_6H_4COPr^i$ (yield 72%) and a small amount (4%) of the corresponding *para*-isomer were formed.

A similar procedure starting from $AlBr_3$ (0.62 g, 2.3 mmol), CBr_4 (0.38 g, 1.15 mmol), and *p*-$ClC_6H_4SiMe_3$ (0.18 g, 0.97 mmol) in the presence of a propane—CO mixture gave 0.174 g (0.95 mmol) of *p*-$ClC_6H_4COPr^i$ (yield 97%); the *meta*-isomer was not present.

Reaction with *n*-butane (general procedure). $AlBr_3$ (1.0 g, 3.7 mmol), CBr_4 (0.62 g, 1.85 mmol), and CH_2Br_2 (1 mL) were placed in a two-necked round-bottomed flask (50 mL) equipped with a magnetic stirrer. The homogeneous solution that formed was cooled with stirring to −20 °C. After 10 min, liquid *n*-butane (1 mL, 0.6 g, 10 mmol) was added, the flask contents were stirred for 1 h under a small pressure of CO, and then *m*-$ClC_6H_4SiMe_3$ (0.27 g, 1.47 mmol) was added. The reaction mixture was stirred for 15 min at −20 °C and for 0.5 h at 0 °C, then EtOH (3 mL) was added, and the mixture was treated with water (20 mL) after another 30 min. The organic products were extracted with CH_2Br_2, and the extracts were dried with $MgSO_4$ and analyzed by GC using benzophenone as the internal standard. According to GC data, 0.142 g (0.73 mmol) of *m*-$ClC_6H_4COCH(Me)Et$ (yield 50%) was formed.

Reaction with cycloalkanes (general procedure). A mixture of anhydrous $AlBr_3$ (2 mmol) and CCl_4 (1 mmol) in CH_2Br_2 (0.5 mL) was stirred for 5 min on a magnetic stirrer. The flask containing the reaction mixture was cooled with liquid nitrogen, and 5 mmol of cyclopentane (or 1.2—2.0 mmol of cyclohexane or methylcyclopentane) was added. The reaction flask was again cooled, evacuated, and connected to a system for feeding CO at atmospheric pressure. The reaction mixture was stirred for 1 h at 0 °C on a magnetic stirrer, a silane (1 mmol) was added, and the mixture was stirred for an additional 15—30 min at the same temperature. The reaction mixture was treated with EtOH (1 mL), and a standard (nonan-2-one or cyclododecanone) was added. The mixture was poured into cold water and extracted with ether. The organic layer was washed with a $NaHCO_3$ solution and water and then dried with Na_2SO_4. The results of the experiments are given in Table 1.

***m*-Chlorophenyl isopropyl ketone.** MS, *m/z* (I_{rel} (%)): 182 [M$^+$] (12), 139 (100), 111 (49), 76 (8), 75 (30), 51 (10), 50 (15). ^{1}H NMR, δ: 7.91 (t, 1 H, *J* = 1.8 Hz); 7.82 (dt, 1 H, *J* = 7.8 Hz, 1.4 Hz); 7.52 (ddd, 1 H, *J* = 7.9 Hz, 1.1 Hz, 1.1 Hz); 7.42 (t, 1 H, *J* = 7.8 Hz); 3.49 (m, 1 H, *J* = 6.8 Hz); 1.18 (d, 1 H, *J* = 6.8 Hz).

***p*-Chlorophenyl isopropyl ketone.** MS, *m/z* (I_{rel} (%)): 182 [M$^+$] (5), 139 (100), 111 (28), 76 (6), 75 (20), 51 (11), 50 (8). ^{1}H NMR, δ: 7.87 (d, 2 H, *J* = 8.5 Hz); 7.43 (d, 2 H, *J* = 8.5 Hz); 3.49 (m, 1 H, *J* = 6.8 Hz); 1.16 (d, 6 H, *J* = 6.8 Hz).

But-2-yl *m*-chlorophenyl ketone. MS, *m/z* (I_{rel} (%)): 196 [M$^+$] (3), 168 (6), 161 (6), 139 (100), 111 (28), 76 (6), 75 (17), 5 (11). ^{1}H NMR, δ: 7.89 (t, 1 H, *J* = 1.8 Hz); 7.80 (dt, 1 H, *J* = 7.8 Hz, 1.4 Hz); 7.53 (ddd, 1 H, *J* = 7.8 Hz, 1.1 Hz, 1.1 Hz); 7.43 (t, 1 H, *J* = 7.8 Hz); 2.2 (m, 2 H); 1.15 (d, 3 H, *J* = 6.9 Hz); 0.86 (t, 3 H, *J* = 7.4 Hz).

Acetylcyclopentane. MS, *m/z* (I_{rel} (%)): 112 [M$^+$] (31), 97 (9), 71 (53), 69 (67), 68 (24), 43 (100), 41 (69).

Propionylcyclopentane. MS, *m/z* (I_{rel} (%)): 126 [M$^+$] (5), 97 (11), 70 (7), 69 (100), 67 (12), 43 (6), 41 (75).

***m*-Chlorophenyl cyclopentyl ketone.** MS, *m/z* (I_{rel} (%)): 208 [M$^+$] (5), 173 (17), 167 (16), 141 (35), 139 (100), 111 (30), 75 (19), 69 (13), 67 (15). ^{1}H NMR, δ: 8.29 (t, 1 H, *J* = 2.1 Hz, 2.1 Hz); 8.19 (dt, 1 H, *J* = 7.4 Hz, 2.1 Hz, 1.1 Hz); 7.89 (ddd, 1 H, *J* = 7.4 Hz, 2.1 Hz, 1.1 Hz); 7.77 (t, 1 H, *J* = 7.4 Hz, 7.4 Hz).

***p*-Chlorophenyl cyclopentyl ketone.** MS, *m/z* (I_{rel} (%)): 208 [M$^+$] (5), 167 (13), 141 (32), 139 (100), 113 (6), 111 (23), 75 (15), 69 (6). ^{1}H NMR, δ: 7.90 (m, 2 H, *J* = 8.6 Hz); 7.43 (m, 2 H, *J* = 8.6 Hz).

Cyclopentyl *m*-tolyl ketone. MS, *m/z* (I_{rel} (%)): 188 [M$^+$] (16), 173 (1), 147 (6), 120 (10), 119 (100), 91 (40), 65 (13), 55 (5), 51 (13).

Cyclopentyl *p*-tolyl ketone. MS, *m/z* (I_{rel} (%)): 188 [M$^+$] (7), 173 (5), 147 (7), 120 (11), 119 (100), 91 (35), 65 (13), 55 (4). ^{1}H NMR, δ: 8.25 (d, 2 H, *J* = 8 Hz); 7.64 (d, 2 H, *J* = 8 Hz).

Acetylcyclohexane. MS, *m/z* (I_{rel} (%)): 126 [M$^+$] (20), 111 (7), 108 (2), 97 (2), 83 (55), 71 (31), 67 (18), 55 (100).

1-Acetyl-1-methylcyclopentane. MS, m/z (I_{rel} (%)): 126 [M^+] (7), 111 (3), 108 (2), 95 (1), 83 (100), 82 (30), 81 (7), 79 (4).

Cyclohexyl *m*-tolyl ketone. MS, m/z (I_{rel} (%)): 222 [M^+] (14), 187 (28), 169 (11), 167 (24), 154 (16), 141 (59), 140 (14), 139 (100).

Cyclohexyl *p*-tolyl ketone. MS, m/z (I_{rel} (%)): 222 [M^+] (9), 187 (17), 169 (7), 167 (16), 154 (12), 141 (53), 140 (12), 139 (100), 108 (2), 95 (1), 83 (100), 82 (30), 81 (7), 79 (4).

Cyclopentyl *p*-methoxyphenyl ketone. MS, m/z (I_{rel} (%)): 204 [M^+] (6), 173 (6), 137 (7), 135 (100), 107 (5), 92 (8), 77 (10), 64 (7), 55 (4). ^{1}H NMR, δ: 7.94 (m, 2 H, J = 9.0 Hz); 6.94 (m, 2 H, J = 9.0 Hz).

Cyclopentyl *p*-(trimethylsilylmethyl)phenyl ketone. MS, m/z (I_{rel} (%)): 260 [M^+] (23), 245 (4), 191 (22), 155 (4), 75 (6), 73 (100), 45 (10), 41 (8).

Cyclopentyl [*p*-dimethyl(ethoxy)silylmethyl]phenyl ketone. MS, m/z (I_{rel} (%)): 290 [M^+] (22), 244 (18), 170 (18), 103 (100), 75 (49), 59 (20), 45 (10), 41 (19).

Cyclopentyl [*p*-dimethyl(isopropoxy)silylmethyl]phenyl ketone. MS, m/z (I_{rel} (%)): 304 [M^+] (14), 261 (8), 117 (33), 104 (4), 75 (100), 69 (5), 45 (10), 41 (19).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-33255, 96-15-97341, and 97-03-32986) and the U.S. Civilian Research and Development Foundation (Grant CRDF RC1-274, prop. 506).

* * *

The authors of this paper were lucky to have been working together with Mark Efimovich Vol'pin, one of them for 40 years, some for 20 years, others for much shorter periods. But even those who have spent a rather short time in his laboratory could not but feel the scale of this scientist. Vol'pin was endowed with a rare intuition and had the will to utter his most fantastic ideas in such a way as to be heard. His interests ranged very widely, and his curiosity was infinite. He was never bound by the limits of any narrow direction of chemistry or even any single field of science. He took interest only in big problems, and he always suggested simple and unexpected solutions. Being quite free in his creative work, he also gave his colleagues a lot of freedom, leaving to himself the role of an arbiter and a producer, who at a dress rehearsal just slightly changes the make-up, and then, on finishing a play, suddenly switches the troupe to something quite different, completely changing the play style and the scenery. The present work was performed without Vol'pin, but we constantly felt his appraising look.

References

1. (a) G. A. Olah, G. K. S. Prakash, and J. Sommer, *Superacids*, Wiley-Interscience, New York, 1985; (b) G. A. Olah and G. K. S. Prakash, in *The Chemistry of Alkanes and Cycloalkanes*, Part 13, Eds. S. Patai and Z. Rappoport, Wiley-Interscience, Chichester, 1992, 624; (c) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1995, **13/14**, 1393.
2. (a) *Activation of Saturated Hydrocarbones by Transition Metal Compounds*, Ed. A. E. Shilov, Reidel, Dordrecht, 1985; (b) *Activation and Functionalization of Alkanes*, Ed. C. L. Hill, Wiley-Interscience, New York, 1989; (c) B. A. Arndtsen, R. G. Bergman, T. A. Mobley, and T. H. Peterson, *Acc. Chem. Res.*, 1995, 28, 154.
3. H. Mimoun, in *Comprehensive Coordination Chemistry*, Eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, New York, 1987, 6.
4. I. S. Akhrem, A. V. Orlinkov, and M. E. Vol'pin, *Usp. Khim.*, 1996, **65**, 920 [*Russ. Chem. Rev.*, 1996, **65**, 849 (Engl. Transl.)].
5. I. Akhrem, A. Orlinkov, and M. Vol'pin, *J. Chem. Soc., Chem. Commun.*, 1993, 671.
6. I. S. Akhrem, A. V. Orlinkov, L. V. Afanas'eva, E. I. Mysov, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1208 [*Russ. Chem. Bull.*, 1996, **45**, 1148 (Engl. Transl.)].
7. I. S. Akhrem, A. V. Orlinkov, L. V. Afanas'eva, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1214 [*Russ. Chem. Bull.*, 1996, **45**, 1154 (Engl. Transl.)].
8. I. Akhrem, S. Bernadyuk, and M. Vol'pin, *Mendeleev Commun.*, 1993, 188.
9. S. Z. Bernadyuk, I. S. Akhrem, and M. E. Vol'pin, *Mendeleev Commun.*, 1994, 183.
10. I. Akhrem, I. Churilova, S. Bernadyuk, and M. Vol'pin, *Tetrahedron Lett.*, 1996, **37**, 5775.
11. A. Orlinkov, I. Akhrem, S. Vitt, and M. Vol'pin, *Tetrahedron Lett.*, 1996, 3363; A. Orlinkov, I. Akhrem, L. Afanas'eva, E. Mysov, and M. Vol'pin, *Mendeleev Commun.*, 1997, 61.
12. M. Koch and W. Haaf, *Org. Synthesis*, 1964, **40**, 1; M. Koch and W. Haaf, *Angew. Chem.*, 1960, **72**, 628.
13. I. Akhrem, *Catal. Lett.*, 1998, in press.
14. A. Yu. Yakubovich and G. V. Motsarev, *Dokl. Akad. Nauk SSSR*, 1953, **88**, 87 [*Dokl. Chem.*, 1953 (Engl. Transl.)].
15. K. Dey, C. Eaborn, and D. R. M. Walton, *Organomet. Chem. Synthesis*, 1970/71, **1**, 151.
16. G. A. Olah, Tse-Lok Ho, G. K. S. Prakash, and B. G. B. Gupta, *Synthesis*, 1977, **10**, 677.

Received October 29, 1997