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Organic Chemistry

Functionalization of alkanes and cycloalkanes by superelectrophiles
15.* Carbonylation of cycloheptane, cyclooctane, and isomeric monoalkylcyclohexanes with CO in the presence of $CBr_4 \cdot 2AlBr_3$ to form individual esters of tertiary carboxylic acids of the cyclohexane series

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Cycloheptane, methylcyclohexane, cyclooctane, and ethylcyclohexane were selectively carbonylated with CO. The reactions of cycloalkanes with CO at −40 °C in the presence of the superelectrophilic system $CBr_4 \cdot 2AlBr_3$ in CH_2Br_2 followed by treatment of the reaction mixtures with alcohols afforded esters of 1-methylcyclohexanecarboxylic acid (in the reactions of cycloheptane and methylcyclohexane) or esters of 1-ethylcyclohexanecarboxylic acid (in the reactions of cyclooctane and ethylcyclohexane) in 70—80% yields with respect to $CBr_4 \cdot 2AlBr_3$. The reaction of 1,3-dimethylcyclohexane at −40 °C and the reactions of cyclooctane and ethylcyclohexane and at −20 °C proceeded nonselectively to form four isomeric esters $C_8H_{15}COOR$.

Key words: tetrabromomethane, aluminum bromide, superelectrophiles, cycloheptane, methylcyclohexane, cyclooctane, ethylcyclohexane, carbon monoxide, esters of 1-alkylcyclohexanecarboxylic acids, functionalization, carbonylation.

The discovery of new systems which activate alkanes under mild conditions[2] gave impetus to extensive studies on the synthesis of organic compounds from accessible alkanes and cycloalkanes. Of one-step functionalization reactions of saturated hydrocarbons, the reactions with CO have considerable potential for organic synthesis.[3] The insertion of CO into nonactivated C—H bonds of hydrocarbons was carried out using transition metal complexes,[2c,d,4] protic[5] and aprotic superacids,[1a—d,2e] and radical species.[6] However, only a limited number of alkanes and cycloalkanes have been subjected to selective carbonylation. The selectivities of the reactions of saturated hydrocarbons decrease as the length of the hydrocarbon chain increases, which is associated with the increase in the number of C—H bonds possessing close reactivities. In addition, long-chain carbenium ions, which are intermediates in electrophilic transformations of saturated hydrocarbons, are more readily subjected to fragmentation than their lower homologs, which results in low selectivities of the carbonylation reactions. The stabilities of alkyl radicals involved in radical reactions and of M—C bonds in organometallic

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* For previous communications, see Ref. 1.

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complexes, which are responsible for carbonylation in the presence of transition metal complexes, change in the same direction.

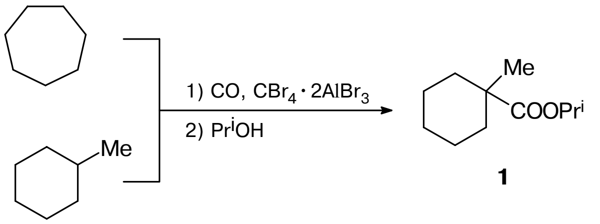
A decrease in selectivity with the increase in the length of the hydrocarbon chain can be exemplified by the reactions[5c] of *n*-alkanes C_6—C_8 with CO in a HF—SbF_5 medium. Carbonylation of hexane followed by hydrolysis of the reaction mixture afforded C_7-acids with secondary and tertiary radicals and a mixture of lower carboxylic acids with the total number of carbon atoms from three to six. Under the same conditions, heptane and octane gave exclusively destructive carbonylation products, *viz.*, C_5- and C_6-acids.[5c]

The selectivity of carbonylation of alkanes and cycloalkanes would be expected to be higher in reactions involving systems which exhibit high activity at low temperatures. Indeed, under these conditions, fragmentation of carbenium ions as well as decarbonylation of the resulting acylium cations are suppressed.[7] It is known that low temperature is favorable for the formation of branched structures.[8] Hence, one would expect that the reactions of saturated hydrocarbons with CO in the presence of powerful superelectrophiles at low temperatures will afford tertiary carboxylic acids or their derivatives. It should be noted that the reactions involving highly active systems proceed in high yields over a short period in the presence of equimolar amounts of electrophiles as well. Reduction of the latter with hydrocarbons leads to a decrease in superelectrophilicity of the system, which is favorable for preservation of functionalization products. On the contrary, the reactions with less reactive electrophiles proceed slowly at higher temperatures and require an excess of an electrophilic reagent,[5] *i.e.*, the electrophilicity of the system changes only slightly in the course of the reaction. It is known that superelectrophilic systems containing polyhalomethanes in combination with aluminum bromide can efficiently generate carbenium ions from saturated hydrocarbons[9] and initiate selective carbonylation of ethane,[1a] propane,[1h] butane, and pentane,[1b] which prompted us to examine the possibility of selective carbonylation of cycloalkanes C_7—C_8 and isomeric cyclohexanes under the action of these systems.

Results and Discussion

At the temperature from −20 to −40 °C, the reaction of cycloheptane with CO in the presence of the superelectrophilic system $CBr_4{\cdot}2AlBr_3$ (S) followed by treatment of the reaction mixture with Pr^iOH gave rise to the only carbonylation product, *viz.*, ester **1** (Scheme 1).

Scheme 1

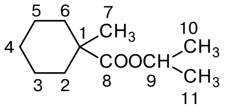


The same product was obtained from methylcyclohexane (Table 1). The mass spectrum of ester **1**

Table 1. Carbonylation of cycloalkanes under the action of CO (1 atm.) initiated by the $CBr_4{\cdot}2AlBr_3$ system (S) in a solution in CH_2Br_2

Run	Cycloalkane RH	[RH] : [S]	*T*/°C	*t*/h	Products of carbonylation and subsequent alcoholysis with Pr^iOH[a]	Yield (mol.%)[b]
1	Cycloheptane	1 : 1	−20	0.5	**1**	36
2	*Ditto*	1 : 1	−40	1	**1**	40
3	» »	1 : 1	−40	2	**1**	82
4	Methylcyclohexane	1 : 1	−40	0.5	**1**	67
5	*Ditto*	1.2 : 1	−40	1	**1**	74
6	Cyclooctane	2 : 1	−20	0.5	**3a** + **3b** + **3c** + **2** (5 : 3 : 4 : 1)	74
7	*Ditto*	2 : 1	−20	0.7	**3a** + **3b** + **3c** + **2** (4 : 2 : 4 : 1)	46
8	» »	2 : 1	−20	1	**3a** + **3b** + **3c** + **2** (3 : 2 : 3 : 1)	47
9 [c]	» »	1 : 1	−30	1	**3a** + **3b** + **3c** + **2** (5 : 3 : 4 : 1)	27
10 [d]	» »	1.2 : 1	−40	1	**3a** + **3b** + **3c** + **2** (11 : 6 : 1 : 5)	73
11	» »	1.2 : 1	−40	0.5	**2**	67
12	» »	1.2 : 1	−40	1	**2**	68
13 [c]	» »	1 : 1	−40	1	**2**	48
14 [e]	» »	1 : 1	−40	2	**2**	40
15	Ethylcyclohexane	1.2 : 1	−40	1	**2**	69
16	1,3-Dimethylcyclohexane	1 : 1	−40	0.5	**3a** + **3b** + **3c** + **2** (11 : 5 : 8 : 1)	90

[a] The ratio of the isomers is given in parentheses in order of increasing retention time; ester **2** has the largest T_R.
[b] With respect to S.
[c] The $CBr_4{\cdot}3AlBr_3$ system was used instead of $CBr_4{\cdot}2AlBr_3$.
[d] The experiment was carried out under a CO pressure of 30 atm.
[e] The $CCl_4{\cdot}3AlBr_3$ system was used instead of $CBr_4{\cdot}2AlBr_3$.

Table 2. The ^{1}H and ^{13}C NMR spectroscopic data for ester  (**1**)

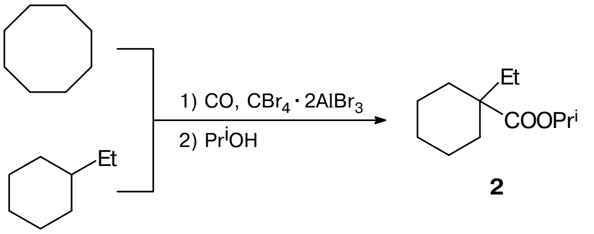
Atom	δ (*J*/Hz)			
	^{1}H		^{13}C	
	Experiment	Calculations	Experiment	Calculations
C(7)H_3	1.10 (s)	1.05	26.50	25.3±3.4
C(10)H_3, C(11)H_3	1.29 (d, ^3J = 6.4)	1.31	21.71	21.9±0.1
C(2)H_2, C(6)H_2	1.10—2.10 (m)	1.23—1.78	35.49	35.5±0.4
C(3)H_2, C(5)H_2	1.10—2.10 (m)	1.23—1.78	23.19	21.6±1.0
C(4)H_2	1.10—2.10 (m)	1.23—1.78	25.71	25.7±1.5
C(9)H	5.00 (septet, ^3J = 6.4)	4.80	66.84	68.5±0.4
C(1)	—	—	42.85	43.0±3.0
C(8)	—	—	176.74	178.7±1.4

(*m/z* (I_{rel} (%)): 184 $[M]^+$ (3), 142 (11), 97 (95), 96 (15), 87 (25), 81 (20), 69 (12), 67 (13), 55 (100)) and the ^{1}H and ^{13}C NMR spectra presented in Table 2 prove the structure of compound **1**. The chemical shifts of the signals observed in the NMR spectra of the esters synthesized were compared with those calculated using the ACD/C- and ACD/H-NMR programs.

Carbonylation of cycloheptane and methylcyclohexane proceeded rather smoothly; bromides $C_7H_{13}Br$ were obtained as by-products in 5—20% yields. These compounds were identified as bromides based on the GLC/MS data, *viz.*, from the positions of the peaks in the chromatograms and from the fact that the mass spectra have the fragmentation ion peaks $[M - Br]^+$ (*m/z* 97) and $[M - HBr]^+$ (*m/z* 96) and rather intense ion peaks at *m/z* 79—82.

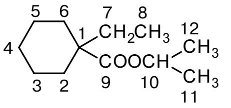
At −40 °C and 1 atm. of CO, cyclooctane also gave virtually the only carbonylation product after alcoholysis, *viz.*, ester **2**, in ~70% yield (Scheme 2; see Table 1).

Scheme 2



The mass spectrum of ester **2**, *m/z* (I_{rel} (%)): 198 $[M]^+$ (5), 170 (10), 156 (15), 127 (15), 111 (90), 110 (51), 109 (13), 101 (51), 81 (50), 69 (10), 57 (17), 55 (81), 53 (16). The experimental and calculated ^{1}H and ^{13}C NMR spectroscopic data for ester **2** are given in Table 3.

The transformation products of cyclooctane also contained a mixture of isomeric bromides $C_8H_{15}Br$ whose yield varied from 10 to 30% depending on the reaction conditions. These isomers were identified as cycloalkyl bromides based on the GLC/MS data. The isomers were localized in a narrow chromatographic zone and the mass spectra of each isomer have intense fragmentation

Table 3. The ^{1}H and ^{13}C NMR spectroscopic data for ester  (**2**)

Atom	δ (*J*/Hz)			
	^{1}H		^{13}C	
	Experiment	Calculations	Experiment	Calculations
C(8)H_3	0.93 (t, ^3J = 8.0)	0.83	8.41	9.6±1.2
C(11)H_3, C(12)H_3	1.22 (d, ^3J = 6.0)	1.31	21.75	21.9±0.1
C(2)H_2, C(6)H_2	1.00—2.10 (m)	1.10—1.80	33.82	34.8±4.0
C(3)H_2, C(5)H_2	1.00—2.10 (m)	1.10—1.80	23.30	21.7±0.8
C(4)H_2	1.00—2.10 (m)	1.10—1.80	26.09	26.6±1.0
C(7)H_3	1.00—2.10 (m)	1.10—1.80	33.40	28.0±4.9
C(10)H	5.00 (septet, ^3J = 6.0)	4.86	66.66	68.5±0.4
C(1)	—	—	46.93	47.3±2.5
C(9)	—	—	175.59	178.1±1.4

ion peaks at *m/z* 111 $[M - Br]^+$ and 110 $[M - HBr]^+$ and rather intense ion peaks at *m/z* 79—82 (Br, HBr) characteristic of bromides.

GLC/MS analysis showed that the reactions of cyclooctane taken in an excess with respect to the superelectrophile afforded isomeric cycloalkanes C_8H_{16}, which were identified as 1,3-dimethylcyclohexane (the major component), 1,2- and 1,4-dimethylcyclohexanes, ethylcyclohexane, and unconsumed cyclooctane based on the NBS 75K library search. Two isomeric hydrocarbons C_8H_{14} were also present in small amounts. The use of a higher excess of $AlBr_3$ in the CBr_4—$nAlBr_3$ system (n was changed from 2 to 3) led to a decrease in the yield of ester **2** and an increase in the yield of bromides.

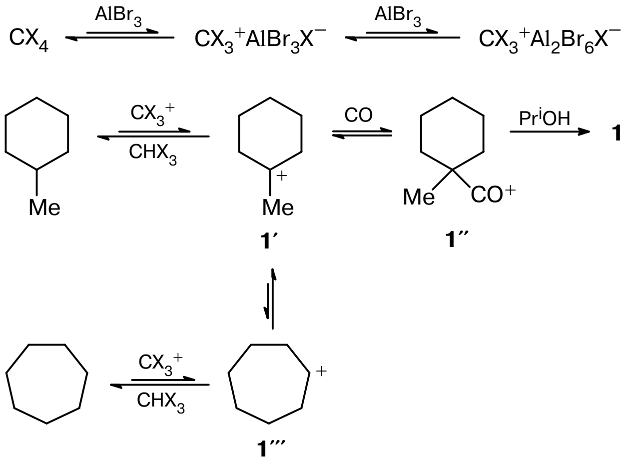
Ethylcyclohexane behaved analogously to cyclooctane and also gave (at −40 °C) ester **2** with high selectivity and in similar yield (see Scheme 2, Table 1).

Unlike methylcyclohexane and cycloheptane whose reactions with CO proceeded selectively both at −40 °C and −20 °C, cyclooctane gave a mixture of four isomeric esters $C_8H_{15}COOPr^i$ in a ratio of 5 : 3 : 4 : 1 (GLC/MS) even at −30 °C, ester **2** being formed in the lowest yield (~8% of the total yield of the mixture of isomers). Based on the data from mass spectrometry, the other three isomers, which were observed along with ester **2** in the same chromatographic zone, have presumably the structures of esters of 1,2-, 1,3-, and 1,4-dimethylcyclohexanecarboxylic acid (**3**). This conclusion was based on the character of the mass spectra of the isomers. These spectra have molecular ion peaks and similar sets of fragmentation ion peaks, which differ only in intensities (see Experimental). The character of fragmentation of these compounds is in complete agreement with the presence of the $COOPr^i$ group (the presence of ion peaks at *m/z* 156 $[M - C_3H_6]^+$, 111 $[M - COOPr]^+$, 87 $[COOPr]^+$, *etc.*). The fact that the mass spectra of isomers **3** contain no fragmentation ion peaks at *m/z* 170 $[M - C_2H_4]^+$ (unlike the mass spectrum of ester **2**) characteristic of the McLafferty rearrangement gives grounds to exclude structures containing the ethyl group in the cycloalkyl fragment. Hence, we had actually to choose between dimethylcyclohexane and trimethylcyclopentane derivatives. We rejected the fact that esters **3** belong to the trimethylcyclopentane series based on the published data on their low thermodynamical stabilities as compared to those of isomeric cyclohexane compounds. The assignment of esters **3** to dimethylcyclohexane derivatives is consistent with the formation of analogous isomers upon carbonylation of 1,3-dimethylcyclohexane (see below).

The reaction of cyclooctane with CO at −20 °C gave rise to the same four isomers whose ratio depended only slightly on the reaction time (0.5—1 h), the content of ester **2** being only 8—11% of the total weight of the mixture of esters. The reaction of cyclooctane with CO at −40 °C under a CO pressure of 30 atm. afforded (in a total yield of 73%) a qualitatively similar mixture of the same isomeric esters containing ~20% of ester **2**. Bromides were obtained as by-products in 27% yield. A decrease in selectivity of carbonylation as the pressure of CO is increased has been described in the literature[10] and has been attributed to rapid nonselective capture of all carbocations in the reaction mixture in the presence of an excess of CO in the system. By contrast, only carbenium ions, which are predominantly present in the reaction mixture, are involved in the reaction if CO is deficient.

The tertiary methylcyclohexyl cation (**1′**), which is a precursor of acylium cation **1″** preceding ester **1** (Scheme 3), is generated from cycloheptane and methylcyclohexane due to its substantially higher stability as compared to the isomeric secondary cation **1‴** (the difference in the energies is ~10 kcal mol^{-1}).[7]

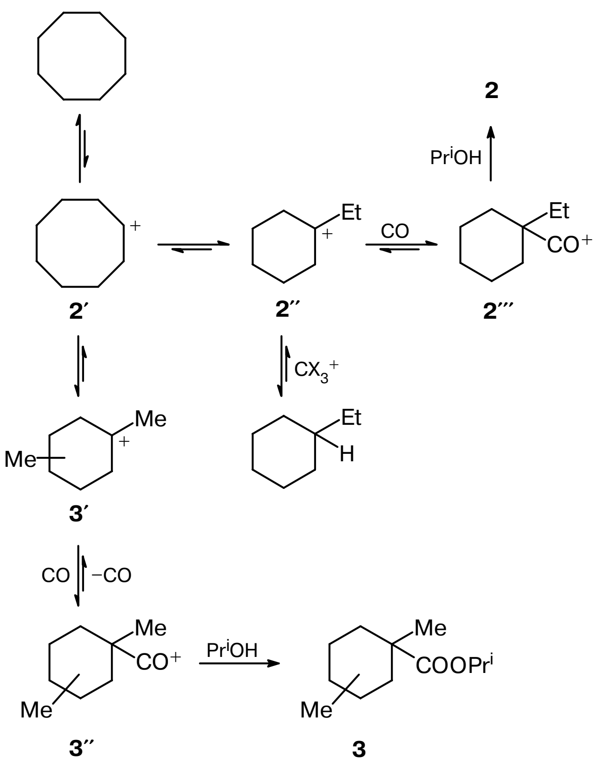
Scheme 3



The reaction of cyclooctane with an electrophile affords the cyclooctyl cation (**2′**), which undergoes isomerization into more stable tertiary carbenium ions to give a series of dimethylcyclohexyl cations (**3′**) and the ethylcyclohexyl cation (**2″**). The addition of CO to cations **3′** and **2″** yields acylium cations **3″** and **2‴**, which are transformed into esters **3** and **2**, respectively, under the action of Pr^iOH (Scheme 4).

Semiempirical PM3 quantum-chemical calculations demonstrated that **2″** is the most stable cation among all the isomeric cations of the cyclohexane series. The difference between the energy of the formation of cation **2″** (ΔH_f = 150.5 kcal mol^{-1}) and that of equally stable dimethylcyclohexyl cations **3′** (ΔH_f = 148.4 kcal mol^{-1}) is 2.1 kcal mol^{-1}. It is known that a decrease in the temperature is favorable for the shift of the equilibrium to the most stable cation.[7,8] This fact accounts for the selective formation of ester **2** from cyclooctane at −40 °C. At the same time, the resistance of the acylium cations to decarbonylation decreases as the stability of the derived carbenium ions increases.[8,11] Cation **2‴** (see Scheme 4) is less resistant to decarbonylation than isomeric ions **3″** producing less stabilized carbocations **3′**.

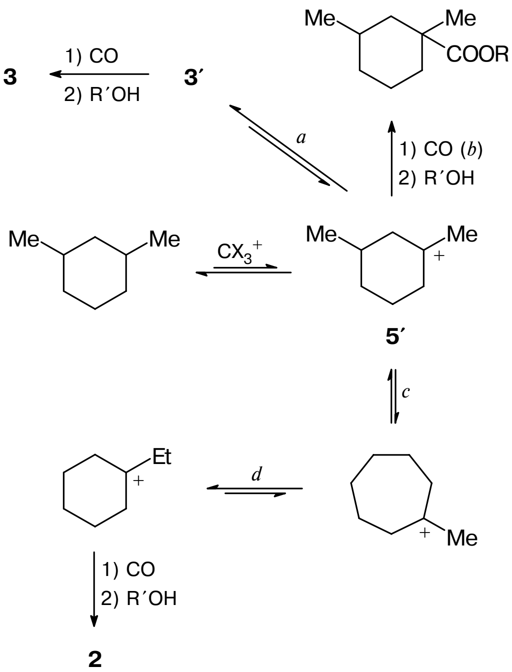
Scheme 4



At −40 °C, acylium cations **2‴** and **3″** are apparently stable. As the temperature is raised from −40 to −30 °C, the rate of decarbonylation of **2‴** becomes noticeable. Since this rate is higher for **2‴** than for acylium cations **3″**, the major carbonylation products (**3**) are formed *via* cations **3′** and **3″**.

Unlike the reactions of unsubstituted cycloalkanes C_7 and C_8 and monoalkylcyclohexanes, carbonylation of 1,3-dimethylcyclohexane proceeded nonselectively even at −40 °C to give a four-component mixture containing esters **2** and **3**, which was identical with that generated from cyclooctane (and ethylcyclohexane) at the temperature in the range from −20 to −30 °C under an atmospheric pressure of CO or at −40 °C under 30 atm. of CO. The ratio of three isomers **3** was very close to that observed in the reactions with cyclooctane performed at −20 °C. However, the content of ester **2** was only 4%. The total yields of the carbonylation and bromination products were 90% and ~10%, respectively. The fact that carbonylation of 1,3-dimethylcyclohexane proceeded nonselectively is apparently associated with higher rates of intramolecular isomerizations of the initially generated 1,3-dimethylcyclohexyl cation **5′** (Scheme 5, reaction *a*) as compared to the rate of the intermolecular addition of CO to cation **5′** (reaction *b*).[5c] Presumably, the formation of small amounts of ester **2** provides evidence that the ring contraction and expansion in the cycloalkyl cations (reactions *c* and *d*) are reversible. The absence of carbonylation products of the methylcycloheptyl cation indicates that the latter undergoes rapid isomerization into cations containing the cyclohexane core.

Scheme 5



Isomerization reactions of cycloalkanes under the action of Lewis acids accompanied by ring contraction are well known.[12] The regularities observed in the present study agree with the published relative rate constants for the contraction of the seven- and eight-membered rings (25 and 16, respectively; the rate constant for the isomerization of ethylcyclopentane into methylcyclohexane is taken as 100%).[13] It should be noted that cycloheptane is quantitatively isomerized into methylcyclohexane, whereas cyclooctane is completely transformed into a mixture consisting of ethylcyclohexane (90%) and dimethylcyclohexanes (10%).

To our knowledge, carbonylation of cycloheptane, cyclooctane, ethylcyclohexane, and 1,3-dimethylcyclohexane has not been reported previously. Carbonylation of methylcyclohexane in a protic superacidic medium (HF—SbF_5) followed by hydrolysis of the reaction mixture afforded[5a] a mixture of 1-methylcyclohexanecarboxylic acid (10%) and isomeric methylcyclohexanoic acids (90%). The reaction was accompanied also by the ring opening to form isomeric hexanes. Carbonylation of cyclooctene afforded 1-ethylcyclohexanecarboxylic acid in 45% yield. This reaction gave rise to high-molecular-weight carboxylic acids as the major products.[14] Carbonylation of methylcyclohexane under the action of CO in 98% H_2SO_4 (or $BF_3 \cdot H_2O$) in the presence of copper or silver salts (as sources of the corresponding metal carbonyls) and olefins or alcohols (as sources of the corresponding carbenium ions) afforded 1-methylcyclohexanecarboxylic acid in 20—70% yields.[15] The drawback of this procedure is the necessity of using copper or silver salts as well as olefins or alcohols which generate the corresponding acids in amounts comparable with the yield of the target product.

To summarize, the use of superelectrophiles based on polyhalomethanes allowed us to carry out selective functionalization of cycloalkanes C_7 and C_8 and isomeric monosubstituted cyclohexanes under the action of CO. Thus, it was demonstrated that the range of saturated hydrocarbons which can be subjected to selective carbonylation is broader than has been assumed before. At low temperature, carbonylation of cycloheptane, cyclooctane, and isomeric monosubstituted cyclohexanes affords compounds of the cyclohexane series containing the carbonyl group at the tertiary carbon atom.

Experimental

Cycloalkanes C_7 and C_8, CBr_4, and $AlBr_3$ (Aldrich) were used without additional purification. Dibromomethane (Aldrich) was dried with calcined $MgSO_4$ and then distilled over CaH_2.

Qualitative and quantitative analysis of the reaction mixtures was carried out by GLC on a Finnigan 9001 chromatograph equipped with a flame ionization detector and a quartz capillary column (30 m × 0.3 mm; DB-5.625 as the stationary phase, helium as the carrier gas) in the linear temperature programming mode. The GLC/MS analysis was performed on an AEI 1073 instrument (70 eV) equipped with an analogous capillary column. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer (400 MHz for ^1H; 100 MHz for ^{13}C) in the JMODECHO mode with Me_4Si as the internal standard.

The reactions of cycloheptane, methylcyclohexane, cyclooctane, ethylcyclohexane, and 1,3-dimethylcyclohexane with CO were carried out under an atmospheric pressure at the temperature from −20 to −40 °C in the presence of $CBr_4 \cdot 2AlBr_3$ or $CCl_4 \cdot 3AlBr_3$ (S) in a solution of CH_2Br_2 or CH_2Cl_2 for 0.5—2 h. The molar ratio [RH] : [S] was varied from 2 : 1 to 1 : 1. The yields of the products were determined by GLC with the use of the internal standard (undecan-2-one) taking into account the correction coefficient.

The samples for ^1H and ^{13}C NMR spectroscopy ($CDCl_3$) were prepared by concentrating ethereal extracts (without the internal standard) *in vacuo*.

Carbonylation of cycloalkanes (general procedure). A solution of a mixture of CBr_4 and anhydrous $AlBr_3$ (taken in a molar ratio of 1 : 2) in CH_2Br_2 (1.5—2 mL per gram of $AlBr_3$) was cooled with stirring to a temperature from −20 to −40 °C and the flask was filled with gaseous CO to which the required amount of cycloalkane was added (see Table 1). The reaction mixture was stirred under conditions given in Table 1. Then Pr^iOH (3 mL per gram of $AlBr_3$) was added and the reaction mixture was heated to 0 °C for 30 min. Then water was added and the organic products were extracted with ether. The extract was washed with water until the reaction became neutral, dried with calcined $MgSO_4$, and analyzed by GLC and GLC/MS.

MS (EI, 70 eV), m/z (I_{rel} (%)) of isomeric esters *cyclo*-$Me_2C_6H_9COOPr^i$ (**3**) (see Table 1, run *6*): **3a**, 198 $[M]^+$ (7), 156 (13), 139 (6), 138 (3), 129 (70), 116 (2), 113 (2), 111 (91), 110 (17), 109 (28), 95 (34), 91 (6), 87 (88), 83 (21), 82 (9), 70 (86), 69 (100), 67 (18), 55 (69); **3b**, 198 $[M]^+$ (9), 156 (21), 139 (5), 138 (4), 129 (5), 115 (3), 112 (8), 111 (95), 110 (24), 109 (14), 95 (21), 91 (67), 87 (24), 83 (20), 81 (12), 70 (82), 69 (100); **3c**, 198 $[M]^+$ (3), 157 (6), 156 (5), 139 (4), 129 (8), 112 (9), 111 (100), 110 (22), 109 (9), 95 (24), 91 (5), 87 (5), 83 (3), 82 (5), 81 (8), 70 (10), 69 (99), 67 (14).

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