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SYNTHESIS OF DIMETHYL ACETALS, DIETHYL ACETALS, AND CYCLIC ACETALS CATALYZED BY AMINOPROPYLATED SILICA GEL HYDROCHLORIDE (APSG·HCL)

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Abstract - The aminopropylated Silica-Gel hydrochloride (APSG·HCl) proved to be an efficient catalyst for the rapid conversion of carbonyl compounds in the corresponding acetals with high yields and in mild and selective conditions. In addition to the obvious advantages offered by heterogeneous catalysis, the present method results very useful when the presence of a weakly-acidic function chemically bonded on the catalyst surface (alkyl ammonium salt) is necessary (compounds which contains functions unstable in acidic media).

The synthesis of acetals from aldehydes and ketones is widely used, and it is carried out by different methods depending on the case: an extensive review on these reactions was recently published.[1]

In the study of this reaction, particular attention was given to the selection of catalysts, and this allowed to select a wide number of those, ranging from conventional acids (sulfuric acid, ethanolic hydrochloric acid, p-toluensulphonic acid, ferric chloride etc.) with or without addition of orthoesters (trimethyl- or triethyl-orthoformate), to acidic resins as, for example, Amberlyst-15[2] or Acidic Montmorillonite Clay K 10[3], and finally to solid superacids, Nafion-H[4] type. Unfortunately, most of the reported methods use reagents and/or conditions which are far too drastic, and therefore not compatible with sophisticated substrates.

In the contest of our researches on polymeric supports for reagents and catalysts, the aminopropylated Silica-Gel hydrochloride (APSG·HCl) proved to be an efficient catalyst for the rapid conversion of carbonyl compounds in the corresponding acetals with high yields and in mild and selective conditions.

The catalyst is easily obtained by derivatizing commercial silica (Si 60, ~ 500 m^2/g) with aminopropyltriethoxysilane (APS) in refluxing toluene following this scheme:

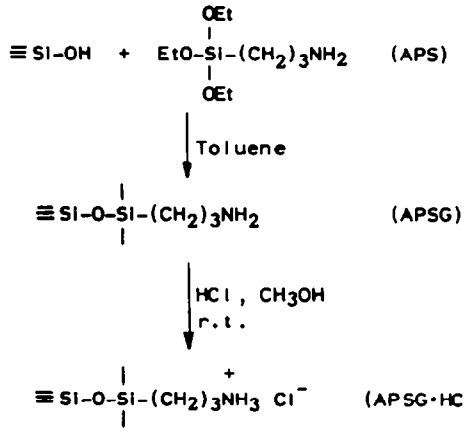
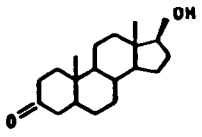
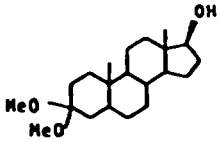
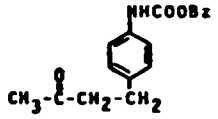
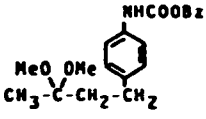
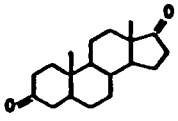
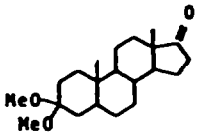
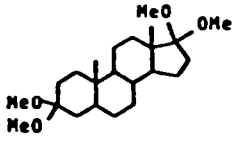
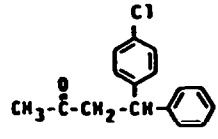
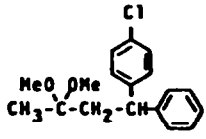
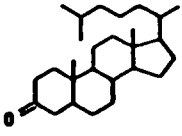
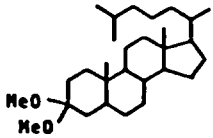
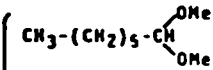
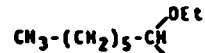
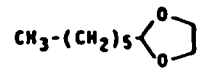
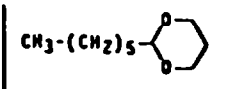
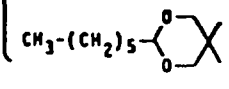
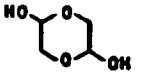
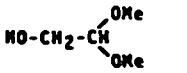
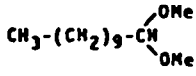
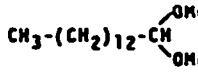
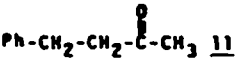
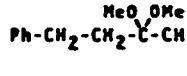
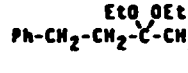
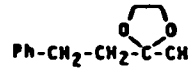
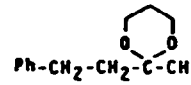
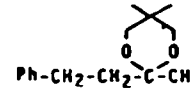
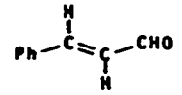
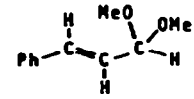
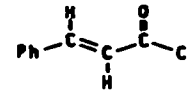
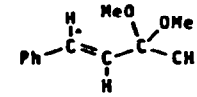
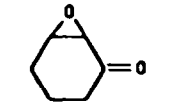
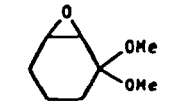


Table 1. Conversion of carbonyl compounds to acetals with APSG·HCl und

Carbonyl compound	Acetal	Reaction procedure Method A Yield [%][a] (reaction time, h)	Method B	m.p.[°C][b,c] or b.p. [°C]/torr $[\alpha]_D^{20}$
 1	 1a	97 (3)		153-194 $[\alpha]_D^{20}$ = +11.39 (C=1.115 $CHCl_3$)
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOEt$ 2	$CH_3-\overset{MeO\ OMe}{\overset{\|}{C}}-CH_2-COOEt$ 2a	80 (15)		161-163/760
 3	 3a	0 (96)	96 (15)	62-63
 4	 4a	76 (20)		128-129 $[\alpha]_D^{20}$ = +100.2 (C=1.293 $CHCl_3$)
	 4b		90 (18)	109-110 $[\alpha]_D^{20}$ = +76.95 (C=1.206 $CHCl_3$)
 5	 5a	0 (96)	98 (15)	143-145/760
 6	 6a	92 (18)		77-78 [f] $[\alpha]_D^{20}$ = +22.93 (C=2.237 $CHCl_3$)
$CH_3-(CH_2)_5-CHO$ 7	 7a	94 (7)		152-154/760
	 7b	96 (8)		204/760
	 7c		93 (8)	137-140/760

experimental conditions A and B. Characterization of the products.

Lit. data or Molecular formula [d] of acetals	IR [e] ν:[cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS int.) δ:[ppm]
m.p. 180-182°C [5] $[\alpha]_{20}^{D}$ = +14 (C=1.68)	3460, 1100, 1040, 870	3.60 (t, J= 7.50 Hz, 1H); 3.17, 3.12 (2s, 6H); 2.00 (bs, 1H, D_2O exchange); 2.10-0.70 (m, 23H); 0.71, 0.80 (2s, 6H)
$C_8H_{16}O_4$ (176.24)	1730, 1310, 1225, 1200, 1165, 1110, 1050	4.15 (q, J = 7.20 Hz, 2H); 3.21 (s, 6H); 2.65 (s, 2H); 1.46 (s, 3H); 1.26 (t, J = 7.20 Hz, 3H)
$C_{20}H_{25}NO_4$ (344.47)	3320, 1720, 1600, 1530, 1220, 1050, 845, 740, 700	7.45-7.00 (m, 10H); 5.15 (s, 2H); 3.17 (s, 6H); 2.73-2.47 (m, 2H); 2.00-1.75 (m, 2H); 1.30 (s, 3H)
- [6]	1735, 1100, 1045	3.17, 3.12 (2s, 6H); 2.50-1.00 (m, 22H); 0.86, 0.83 (2s, 6H)
$C_{23}H_{40}O_4$ (380.63)	1285, 1155, 1105, 1070, 1050	3.18, 3.16, 3.15, 310 (4s, 12H); 2.20-0.90 (m, 22H); 0.87, 0.80 (2s, 6H)
$C_{18}H_{21}ClO_2$ (304.84)	1490, 1220, 1125, 1090, 1050, 840, 750, 695	7.37-7.07 (m, 9H); 4.07 (t, J = 6.75 Hz, 1H); 3.08 (s, 6H); 2.45 (d, J = 6.75 Hz, 2H); 1.00 (s, 3H)
m.p. 79-80°C [6]	1135, 1105, 1045	3.18, 3.13 (2s, 6H); 2.05-0.60 (m, 46H)
b.p. 81-82/20 [7]	1190, 1130, 1055	4.35 (t, J = 5.25 Hz, 1H); 3.30 (s, 6H); 1.75-1.17 (m, 10H); 0.90 (t, J = 6.00 Hz, 3H)
b.p. 204/760 [8]	1460, 1375,1345, 1130, 1060	4.48 (t, J = 5.55, 1H); 3.65, 3.48 (m, 4H); 1.80-1.03 (m, 10H); 1.17 (t, J = 7.12 Hz, 6H); 0.90 (t, J = 6.00 Hz, 3H)
b.p. 93-95/20 [9]	1145, 1120, 1035, 940	4.85 (t, J = 4,50 Hz, 1H); 4.10-3.70 (m, 4H); 1.90-1.07 (m, 10H); 0,90 (t, J = 6.00 Hz, 3H)

Carbonyl compound	Acetal	Reaction procedure Method A Yield [%][a] (reaction time, h)	Method B	m.p.[°C][b,c] or b.p. [°C]/torr $[\alpha]_D^{20}$
	 7d		92 (15)	152-154/760
	 7e		91 (10)	oil
 8	 8a	92 (15)		165-167/760
$CH_3-(CH_2)_9-CHO$ 9	 9a	95 (10)		250-255/760
$CH_3-(CH_2)_{12}-CHO$ 10	 10a	97 (10)		oil
 11	 11a	32 (18)	98 (13)	oil
	 11b	94 (18)		177-179/760
	 11c		95 (10)	oil
	 11d		91 (15)	oil
	 11e		93 (12)	oil
 12	 12a	91 (4)		oil
 13	 13a		96 (20)	oil
 14	 14a	89 (24)		165-167/760

a) Yield of isolated pure product. b) Uncorrected. C) Unless otherwise noted, d) Satisfactory microanalysis obtained: C, ± 0.25; H, ± 0.15; N, ± 0.23 %. those of solid samples in nujol mull. f) Recrystallized from methanol/water.

Lit. data or Molecular formula of acetals [d]	IR [e] ν:[cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS int.) δ:[ppm]
- [10]	1470, 1375, 1240, 1145, 1115, 1000	4.50 (t, J = 4.87 Hz, 1H); 4.25-3.98 (m, 2H); 3.91-3.57 (m, 2H); 2.77-2.37 (m, 1H); 1.70-1.47 (m, 1H); 1.47-1.10 (m, 10H); 0.88 (t, J = 6.00 Hz, 3H)
b.p. 92-93/5 [11]	1465, 1380, 1125, 1050	4.30 (t, J = 5.25 Hz, 1H); 3.55-3.35 (m, 4H); 1.85-1.10 (m, 10H); 1.05-0.75 (m, 9H)
b.p. 58-60/12 [12]	3430, 1195, 1130, 1080, 970	4.42 (t, J = 5.25 Hz, 1H); 3.57 (bt, J = 5.50 Hz, 2H); 3.40 (s, 6H); 2.91 (bt, J = 5.50 Hz, 1H, D_2O exchange)
- [13]	1190, 1130, 1055	4.33 (t, J = 5.40 Hz, 1H); 3.30 (s, 6H); 1.73-1.15 (m, 18H); 0.88 (t, J = 6.00 Hz, 3H)
b.p. 134-136/4 [14]	1190, 1125, 1055	4.35 (t, J = 5.62 Hz, 1H); 3.30 (s, 6H); 1.75-1.10 (m, 24H); 0.88 (t, J = 6.00 Hz, 3H)
$C_{12}H_{18}O_2$ (194.30)	1600, 1450, 1375, 1205, 1120, 1050, 855, 695	7.30-7.15 (m, 5H); 3.17 (s, 6H); 2.77-2.53 (m, 2H); 2.07-1.80 (m, 2H); 1.32 (s, 3H)
b.p. 119-120 [15]	1600, 1450, 1375, 1210, 1130, 1060, 745, 700	7.40-7.00 (m, 5H); 3.48 (q, J = 7.00 Hz, 4H); 2.80-2.53 (m, 2H); 2.10-1.13 (m, 2H); 1.37 (s, 3H); 1.18 (t, J = 7.00 Hz, 6H)
b.p. 141/17 [16]	1600, 1380, 1225, 1145, 1055, 865, 750, 700	7.35-6.97 (m, 5H); 3.88 (bs, 4H); 2.85-2.57 (m, 2H); 2.08-1.80 (m, 2H); 1.33 (s, 3H)
$C_{13}H_{18}O_2$ (206.31)	1600, 1450, 1380, 1370, 1245, 1155, 1090, 850, 755	7.40-7.00 (m, 5H); 3.90 (t, J = 5.55 Hz, 4H); 2.87-2.57 (m, 2H); 2.15-1.87 (m, 2H); 1.85-1.50 (m, 2H); 1.43 (s, 3H)
$C_{15}H_{22}O_2$ (234.37)	1600, 1375, 1255, 1215, 1125, 1090, 860, 750, 700	7.40-7.00 (m, 5H); 3.57-3.40 (2AB, J_{AB} = 10.9 Hz, 4H); 2.93-2.63 (m, 2H); 2.13-1.85 (m, 2H); 1.40 (s, 3H); 1.01 (s, 3H); 0.87 (s, 3H)
- [3]	1600, 1450, 1350, 1190, 1125, 1050, 965, 750, 690	7.50-7.15 (m, 5H); 5.73 (d, J = 16.50 Hz, 1H); 6.13 (dd, J = 16.50 Hz, J = 4.50 Hz, 1H); 4.92 (d, J = 4.50 Hz, 1H); 3.33 (s, 6H)
$C_{12}H_{16}O_2$ (192.28)	1610, 1450, 1240, 1185, 1135, 1045, 745, 690	7.50-7.13 (m, 5H); 6.78 (d, J = 16.50 Hz, 1H); 6.08 (d, J = 16.50 Hz, 1H); 3.20 (s, 6H); 1.43 (s, 3H)
$C_8H_{14}O_3$ (158.20)	1450, 1115, 1055, 930, 900, 850	3.38 (s, 3H); 3.35-3.20 (m, 1H); 3.25 (s, 3H); 3.10 (d, J = 4.20 Hz, 1H); 2.20-1.25 (m, 6H)

solid products were recrystallized from CH_2Cl_2-hexane mixture.
Spectra of liquid samples were recorded as liquid film, whereas

The catalyst could also be obtained by reacting commercial LiChroprep-NH_2^{TM}, 25-40 μm (Merck) with methanolic hydrochloric acid.

The reaction, in our conditions, does not require any preabsorption on the catalyst, as generally observed when different solid acids were used[3], and, in addition, it can be realized under mild conditions.

As regards the effectiveness of the reaction, our results prove that it depends on the nature of the substrate. Actually, sufficiently reactive carbonyl compounds react with alcohol and are transformed in the corresponding dimethyl- or diethyl-acetals, at room temperature, in the presence of the sole catalyst and under stirring (Method A, Experimental part).

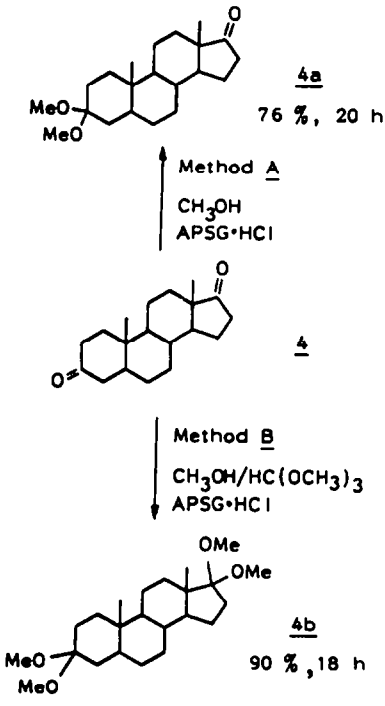
Far lower yields are obtained in the transformation of the same substrates in cyclic acetals; unsatisfactory results are also obtained in reactions run in similar conditions on less reactive carbonyl compounds. In the last two cases, the above procedure has to be modified, adding ethyl- or methyl--orthoformate to favour the removal of water (Method B, Experimental part).

Generally, the reaction was monitored by G.L.C. or H.P.L.C., to optimize the experimental conditions.

Owing to the remarkable mechanical resistance of the particles, the isolation of the reaction product can be easily realized by filtering out the catalyst, the latter being easily regenerated by elution with methanolic hydrochloric acid.

The results obtained with substrates of different nature in addition to the physico--chemical properties of the products, which are never extensively described in the literature, are reported in Table 1.

It is worth remarking that, in some cases, an elevated selectivity of reaction can be obtained by varying the experimental conditions, as can be seen in the following example:



Some of the advantages offered by the present method are shown in Table 2. The reported data show that carbonyl compounds, containing functions easily affected by acidic media, when reacted in our conditions (Method A, APSG·HCl), gave better results in comparison with those obtained by known procedures still using heterogeneous catalysis (e.g. Method A, Amberlyst-15).

The yields of the conversion catalyzed by APSG·HCl are higher than those obtained with the resin Amberlyst-15, which contains a very acidic function (sulfonic group). In the last case, formation of secondary products was detected beside the main one.

For instance, when substrate 2 was transformed in the corresponding acetal 2a, in the presence of Amberlyst-15 as catalyst, the transesterification products methyl-3,3-dimethoxy-butenoate and methylacetoacetate, were isolated in 21% and 3% respectively.

Moreover, the epoxidic function, contained

Table 2

Carbonyl compound	Acetal	Reaction procedure	
		Method A / APSG•HCl	Method A / Amberlyst-15
		yield % (reaction time, h)	
2	2a	80 (15)	67* (10)
4	4a	76 (20)	73 (11)
14	14a	89 (24)	44 (15)

* Compound 2 was reported to be directly transformed in ethyl-3-methoxy-2-butenoate in more drastic conditions [2].

in the compound 14, whereas resulted unaffected in the presence of APSG•HCl, it was opened when Amberlyst-15 was used as catalyst. In this case, the acetal 14a was isolated beside a remarkable amount (49%) of compounds derived from the epoxide ring opening.

Finally, the reaction with APSG•HCl on compound 4 has shown an elevated regioselectivity, as above reported; the two carbonyl functions were selectively transformed giving the corresponding monoacetal 4a or diacetal 4b, by varying the experimental conditions. The diacetal was obtained exclusively by adding methyl orthoformate in the reaction medium (Method B).

The described method represents a valid system for the conversion of carbonyl compounds in the corresponding acetals, mainly for those which contain functions unstable in acidic media. In addition to the obvious advantages offered by heterogeneous catalysis (for instance, the catalyst can be easily filtered out from the reaction mixture), the present method results very useful when the presence of a weakly-acidic function on the catalyst surface (alkyl ammonium salt) is necessary.

The advantage of our procedure can be summarized as follow: possibility of working under extremely mild conditions; absence of transesterification (e.g. compound 2a, Table 1); remarkable selectivity (e.g. compound 4a, Table 1), stability of functions which are unstable in acidic media (e.g. compounds 3a, 14a, Table 1, 2), high yields of conversion and absolute reproducibility of results. Additional advantages offered by the catalyst, because of the nature of the siliceous support, consist particularly: in the mechanical resistance of the catalyst; in the easy regeneration of the resin by elution with methanolic hydrochloric acid and finally in the ease of preparation of the catalyst by derivatizing commercial silica.

EXPERIMENTAL PART

Equipment - Vapor phase chromatography was performed using a Carlo Erba Fractovap 4160 or a Hewlett-Packard Mod. 7620A. Analytical liquid chromatography was performed on a Waters Associates ALC/GPC-202/R 401 chromatograph (Waters Associates, Milford, Ma.,USA) equipped with a U6K universal injector, a Model M6000 and M-45 solvent delivery system, a Model 480 λ_{max} differential UV detector and a Model 401 refractive index (R.I.) detector. IR spectra were recorded with a Perkin-Elmer Model 297 grating spectrophotometer. ^{1}H-NMR spectra were obtained with a Varian EM-390 spectrometer. Chemical shifts are expressed in values (ppm) relative to a Me_4Si internal standard. All m.p.s reported are uncorrected and were determined with Büchi apparatus.

Analytical data (% C, H, and N) were obtained from Mikroanalytisches Laboratorium, Dr F. Pascher, Bonn (Germany). Mass spectra were recorded with a Hewlett-Packard HP5980A spectrometer equipped with a Data System 5870A. $[\alpha]_D^{20}$ were determined with a Perkin-Elmer Model 241 polarimeter.

H.P.L.C. preparative separations were performed on a Miniprep LC (2 cm i.d. column) or a Chromatospac Prep 10 chromatograph (4.0 cm i.d. column), both from Jobin Yvon (Longjumeau, France), equipped with an R.I. detector.

Reagents - The starting carbonyl compounds 1, 2, 4, 6, 7, 8, 9, 10, 11, 12, 13 are commercially available and were used without further purification. Compounds 5[17] and 14[18] were prepared according to the cited references. LiChrosorb-NH_2^{TM}, 25-40 μ were commercially available from Merck.

Preparation of N-carbobenzoxy-4-(3-oxobuthyl)-aniline (3).

This compound is obtained by reacting p-chloromercury-N-carbobenzoxyaniline with methylvinylketone, following the procedure described in the literature[17], yield: 83 %; m.p. 78-79 °C (CH_2Cl_2/hexane).

I.R. (Nujol): ν =3320, 1708, 1698, 1330, 1240, 1070, 820, 745 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 7.55-6.85 (m, 10 H); 5.17 (s, 2H); 3.00-2.50 (m, 4H); 2.07 (s, 3H) ppm. $C_{18}H_{19}NO_3$ (297.38) requires: C, 72.69; H, 6.45; N, 4.71 %. Found: C, 72.51; H, 6.40; N, 4.68 %.

Preparation of the aminopropylated Silica-Gel hydrochloride (APSG·HCl) resin.

a) *Preparation of aminopropylated Silica-Gel (APSG).* 100 g of LiChroprep Si-60 25-40 μ m Merck are suspended in toluene (500 ml) into a three-necked flask provided with a head for distillation, in argon atmosphere. The mixture is then heated to boiling point, and the water contained in the silica gel is entirely eliminated by azeotropic distillation. After cooling, the 3-aminopropyltriethoxysilane (APS) (45 ml in 20 ml toluene) is slowly added under magnetic stirring. After this addition, the mixture is heated to boiling point, the ethanol formed during the reaction is eliminated, then the reflux is maintained for 1 hour. After cooling and filtration over Büchner, the residue is rinsed with dichloromethane, methanol, methanol/water mixture, and with methanol again, finally it is dried-up with an oil pump. The APSG yield is practically quantitative.

b) *Preparation of the hydrochloride (APSG·HCl)*

10.0 g of aminopropylated Silica Gel (APSG), or in alternative LiChroprep-NH_2^{TM} 25-40 μ m, Merck are suspended in methanol (50 ml) added with 10 ml conc. HCl (37 %); after about 20 min of stirring, the mixture is filtered through Büchner, and the collected precipitate is rinsed with methanol (100 ml), and then with dichloromethane (10 ml); finally it is dried-up under vacuum with an oil pump.

Elemental analysis: APSG · HCl Found C, 3.46; H, 1.49; N, 1.35; Cl, 2.97 % equivalent to 0.83 mmol $\sim\!\!\sim NH_3^+Cl^-$/g support.

Regeneration of the resin. The used polymeric catalyst (APSG·HCl) is successively washed with the following solvents: methanol, water, methanol and treated as described above.

Preparation of acetals.

Method "A": (Direct acetalization without removal of water). The carbonyl compound (10.00 mmol) is added to a suspension of APSG·HCl (0.200 g) in alcohol (anhydrous methanol or ethanol) (50 ml) and allowed to react at room temperature and under stirring for the time required for the formation of the corresponding acetals (see Table 1).

In the Method A/Amberlyst-15 the reaction is carried out in the above described conditions on some substrates which are generally unstable in acidic media and, by using Amberlyst-15 as catalyst in a ratio of 100 mg

to 10 mmol of carbonyl compound. The time required for the disappearance of the starting material is reported in Table 2.

Method "B": (Acetalization by the orthoester method, removal by chemical methods of the water formed in the reaction). This procedure is employed both in the preparation of dimethyl- and diethylacetals of lesser reactive carbonyl compounds, and in the formation of cyclic acetals (dioxolanes, dioxanes). The procedure is similar to that of the case described above (Method A), plus the addition of trimethyl- or triethylorthoformate (30.0 mmol), as a dehydrating agent, to the reaction medium. Moreover, in the preparation of cyclic acetals, 50 mmol of the diol has to be added.

The catalyst is filtered and rinsed with the same alcohol used in the reaction; the filtered solutions are collected and distilled under reduced pressure. The residue can be analyzed by gas-chromatography in packed or capillary columns. The following gas-chromatographic conditions were used:

Capillary column: OV-1, 25 m, 0.30-0.32 mm ID Duran Glass, 0.40 μm film thickness, splitter 1:40, Temp. inj. 300°C, FID 300°C, Carrier: helium, 2.0 ml/min. Packed column: 2m x 1/4" O.D. Glass, packed with 10 % Carbowax 20M on 100-120 mesh Supelcoport; Temp. inj. 200°C; detector: flame ionization, 300°C; carrier: helium, 40 ml/min.

The residue can also be analyzed by H.P.L.C. (Column: Hibar SI60, 10 μ). Pure acetals are obtained by fractioned distillation (see Table 1) or by chromatography of the residue on a Silica-Gel open column (SI-60 0.040-0.063 mm) or by preparative H.P.L.C. (LIChroprep SI-60, 15-25 μm), by eluting with the following hexane/ethyl acetate mixtures:

a) Hexane/AcOEt (70/30) v/v for compounds 1a, 3a, 8a;

b) Hexane/AcOEt (90/10) v/v for compounds 2a, 14a;

c) Hexane/AcOET (95/5) v/v for compounds 4a, 4b, 5a, 6a, 7a, 7b, 7c, 7d, 7e, 9a, 10a, 11a, 11b, 11c, 11d, 11e, 12a, 13a.

The reaction mixture, obtained in the preparation of cyclic acetals, contains also small amounts (1.5-6.0 %) of the corresponding dimethyl acetals.

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