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Active Metals from Potassium–Graphite. Air-Oxidized Nickel–Graphite as a New Selective Hydrogenation Catalyst

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Air exposure of Ni-Gr1 affords a modified, less active hydrogenation catalyst (air-oxidized nickel–graphite, Ni-Gr2), owing to a partial oxidation of the metal, which is able to reduce carbon–carbon, carbon–oxygen, and carbon–nitrogen multiple bonds under 30 atm of hydrogen in the temperature range 30–130 °C. A remarkable bond selectivity in the hydrogenation of polyfunctional molecules such as unsaturated carbonyl compounds and β-diketones is observed.

In the foregoing paper we described the preparation of highly dispersed nickel on graphite (Ni-Gr1) by the reaction of potassium–graphite (C_8K) with a solution of the complex bis(1,2-dimethoxyethane)dibromonickel ($NiBr_2 \cdot 2DME$) in tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPTA) solution, and we showed its use "in situ" for the stereospecific semihydrogenation of alkynes at room temperature and atmospheric pressure.[1]

We now report that air exposure of Ni-Gr1 affords a deactivated catalyst (Ni-Gr2), which is able to promote the hydrogenation of a variety of functional groups by the proper choice of the temperature under a hydrogen pressure of 30 atm. This catalyst is not pyrophoric and may be stored in polyethylene bottles virtually unchanged for 4 months, after which catalytic activity slowly decreases.

Results and Discussion

Catalyst Preparation and Use. The preparation of Ni-Gr2 can be accomplished on a large scale by starting from 14–20 g of C_8K and a standard solution of $NiBr_2 \cdot 2DME$ in THF–HMPTA (15/1) under a rigorous argon atmosphere and following the same procedure previously described for Ni-Gr1.[1] The mixture is stirred for 5 h, water is added to destroy possible traces of C_8K for a safe filtration (C_8K is pyrophoric), and the solid phase is filtered, washed with water, methanol, and ether, and finally dried. Filtration and washing are carried out with air exposure, so a partial oxidation of the metal takes place.[2]

Ni-Gr2 is not active under the same conditions in which Ni-Gr1 promotes the hydrogenation of alkynes (room temperature and atmospheric pressure).

All the reactions reported in this paper have been carried out in a stainless-steel autoclave filled with hydrogen at an initial pressure, at room temperature, of 30 atm.

Semihydrogenation of Alkynes. Owing to the great interest devoted to the acetylenic group and for comparison with the precursor catalyst Ni-Gr1, we checked the effectiveness of Ni-Gr2 for the hydrogenation of conjugated and unconjugated alkynes, evaluating the extent of semihydrogenation and the stereospecificity.

Runs performed with 1-hexyn-3-ol in different solvents show that the highest catalytic activity and alkene/alkane ratio are obtained by using THF as solvent (Table I, entry 2). Ni-Gr2 is also active in other protic or dipolar solvents at room temperature, while in cyclohexane it works at 50 °C.

Table II collects the results obtained in the hydrogenation of disubstituted alkynes in THF at 50 °C. The *Z/E* ratio of the corresponding alkenes ranges between 91/9 and 93/7, being generally lower than the corresponding values obtained with Ni-Gr1,[1] except for ethyl phenylpropynoate.

Attempts to improve the Ni-Gr2 performances by adding amines such as ethylenediamine, quinoline, or piperidine failed for a complete loss of catalytic activity.

Side reactions such as double bond migration and water elimination or hydrogenolysis in the case of propargylic alcohols were not observed.

Hydrogenation Reaction of Typical Substrates. In order to test the usefulness of Ni-Gr2 as hydrogenation catalyst, we performed the reduction of representative substrates in methanol (Table III).

In agreement with the results reported with the most common catalysts,[3] the following decreasing order of reactivity toward catalytic hydrogenation was observed: $C{\equiv}C > C{=}C \approx NO_2 > C{=}O > C{\equiv}N$.

Substitution on the carbon–carbon multiple bond clearly affects the reactivity, owing to a more difficult adsorption of the substrate on the catalytic surface. In fact, among alkynes, 1-decyne is converted at 30 °C to a mixture of 1-decene and decane (entry 1, Table III), while 5-decyne requires a temperature of 50 °C to be reduced (entry 2). In the same way, 1-octene and 2-octene are quantitatively hydrogenated at 50 °C in 6 and 24 h, respectively (entries 3 and 4).

On the other hand, conjugation of the multiple bond with an aromatic ring enhances the reaction rate for both alkenes (entries 4 and 5) and ketones (entries 7 and 8).

While palladium, platinum, and nickel are excellent catalysts for the reduction of nitroarenes to amines,[4] Ni-Gr2 proves to be poorly active, probably because the aromatic amine poisons the catalyst. Thus, a high catalyst/substrate ratio is necessary to achieve a 65% conversion of 4-nitro- to 4-amino-1-methoxybenzene (entry 6, Table III).

The reduction of phenylacetonitrile at 120 °C give β-phenylethylamine together with bis(β-phenylethyl)amine, which is formed by the addition of the primary amine to the intermediate imine, followed by loss of ammonia and hydrogenation of the resulting Schiff base[5] (entry 9).

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(1) Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A., preceding paper in this issue.

(2) ESCA analysis (Mg Kα) of the Ni-Gr2 surface showed in the binding energy region of nickel 2p 3/2 electrons a photoemission peak at 960 eV, which was formed by two components separated by a chemical shift of ~2.5 eV in the relative ratio 4/6, ascribed respectively to Ni° and NiO. It is plausible that a layer of nickel oxide covers the metal particles. Ni(II) catalysts supported in organic polymeric matrices have been found active in hydrogenation reactions: Leonard, W. J., Jr.; Holler, H. V. A.; German Offen. 2213485, 1972; *Chem. Abstr.* **1973**, *78*, 44295. Holy, N. L.; Shalvoy, R. *J. Org. Chem.* **1980**, *45*, 1418.

(3) House, O. H. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: 1972; p 9.

(4) Rylander, P. N. "Catalytic Hydrogenation in Organic Synthesis"; Academic Press: New York, 1979; Chapter 7.

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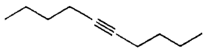
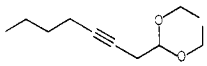
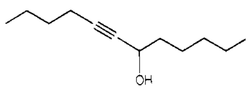
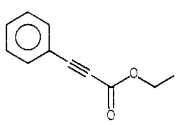
Table I. Hydrogenation of 1-Hexyn-3-ol in Various Solvents

entry[a]	solvent	% conv[b]	% yield[c] alkene	alkane	alkene/alkane ratio
1	acetonitrile	60	73	22	3.32
2	tetrahydrofuran	100	67	29	2.31
3	acetone[d]	60	53	43	1.24
4	methanol	95	45	50	0.90
5	diethyl ether	100	3	91	0.03
6	cyclohexane[e]	100	22	75	0.29

[a] All the reactions were carried out by using 1.75 g of 1-hexyn-3-ol and 0.25 g of Ni-Gr2 (approximate nickel/substrate ratio of 2.2% by weight) in 50 mL of solvent at 30 °C under 30 atm of hydrogen for 6 h. [b] Conversions were evaluated by GC. [c] GC yields (column B, 120 °C) were corrected for the unreacted substrate. [d] No traces of 2-propanol were detected. [e] The reaction was carried out at 50 °C; no hydrogenation took place at 30 °C.

Table II. Hydrogenation of Disubstituted Alkynes

entry	substrate[a] (amt, g)	Ni-Gr2, g	time, h	% conv[b]	% yield[c] alkene	alkane	Z/E[d] ratio
1	 (1.53)	0.28	6	90	60	30	91/9[e]
2	 (1.05)	0.15	15	95	79	10	93/7[e]
3	 (1.96)	0.25	6	96	76	20	92/8
4	PhC≡CPh (1.54)	0.24	10	78	72	10	93/7
5	 (3.16)	0.51	6	92	75	6	96/4

[a] All the reactions were carried out in THF containing 1–2% of water at 50 °C. [b] Conversions were evaluated by GC. [c] GC yields were corrected for the unreacted alkyne. [d] Values based on GC peak area ratios. [e] Values based on GC of corresponding epoxides.

Table III. Hydrogenation of Typical Substrates

entry[a]	substrate (amt, g)	Ni-Gr2, g	time, h	temp, °C	% conv[b]	product (yield, %)[c]
1	1-decyne (1.52)	0.25	6	30	97	1-decene (48)[d] + decane (49)[d]
2	5-decyne (1.54)	0.25	6	50	88	5-decene (54)[d,e] + decane (30)[d]
3	1-octene (1.43)	0.24	6	50	100[f]	octane (96)
4	2-octene (1.47)	0.23	24	50	100[g]	octane (95)
5	ethyl 3-phenylpropenoate (5.25)	0.50	15	50	100	ethyl phenylpropanoate (83)
6	1-methoxy-4-nitrobenzene (2.05)	1.00	15	50	65	1-methoxy-4-aminobenzene (95)
7	2-undecanone (3.28)	0.91	15	90	76	2-undecanol (96)
8	1-phenyl-1-propanone (4.05)	1.25	15	90	100	1-phenyl-1-propanol (98)
9	phenylacetonitrile (3.10)	1.41	6	120	100[h]	β-phenylethylamine (71) + bis(β-phenylethyl)amine (11)

[a] All the reactions were carried out in methanol (50 mL). [b] Conversions were evaluated by GC. [c] Yields refer to pure isolated compounds and are corrected for the unreacted substrate. [d] Yields were evaluated by GC. [e] Z/E ratio 91/9. [f] 100% after 50 h at 50 °C under 5 atm of hydrogen. [g] 88% after 17 h. [h] No reaction occurred at 60 °C.

Ni-Gr2 does not display activity toward the aromatic ring and the ethoxycarbonyl group under the conditions described in Table III.

Selective Hydrogenations of Unsaturated Carbonyl Compounds and β-Diketones. The results obtained in the hydrogenation of some unsaturated carbonyl compounds (Table IV) indicate that Ni-Gr2 exhibits a remarkable bond selectivity, strongly dependent on the temperature. In all cases no hydrogenation takes place at room temperature, but in the range 45–65 °C the aldehydic group of citral (entry 1) and the conjugated carbon–carbon double bonds of α-ionone, β-ionone, carvone, and citral are easily reduced (entries 1, 3, 6, 7).[6] Only at a higher temperature (80–90 °C) is the carbonyl group of α-ionone hydrogenated, while the highly hindered trisubstituted unconjugated double bonds of citral and α-ionone react only at 120–130 °C[7] (entries 2, 4, 5).

Interestingly, a selective reduction of the less hindered carbonyl group of 6-methyl-2,4-heptanedione is obtained

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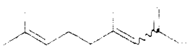
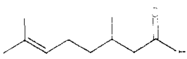
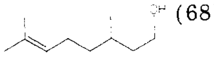
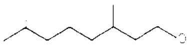
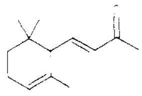
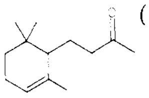
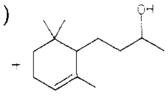
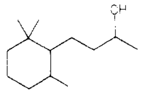
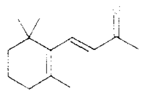
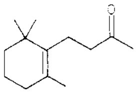
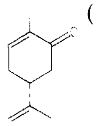
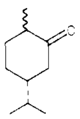
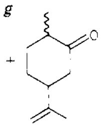
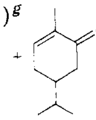
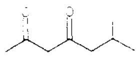
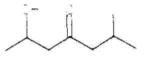
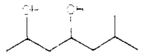
(5) Juday, R.; Adkins, H. *J. Am. Chem. Soc.* **1955**, *77*, 4559.

(6) The selective reduction of the carbon–carbon double bond of conjugated ketones and aldehydes is generally achieved by using palladium catalysts: ref 4, p 51. On the contrary, osmium supported on alumina or charcoal is an excellent catalyst for the reduction of α,β-unsaturated aldehydes to allyl alcohols: Rylander, P. N.; Steele, D. R. *Tetrahedron Lett.* **1969**, 1579.

(7) An elegant route to selective reductions of dienes opposite to those usually achieved can be accomplished by first protecting the less hindered double bond with $C_5H_5Fe(CO)_2^+$, hydrogenating the less reactive bond, and finally decomplexing the olefin by treatment with NaJ in acetone: Nicholas, K. M. *J. Am. Chem. Soc.* **1975**, *97*, 3254.

Table IV. Hydrogenation of Polyfunctional Compounds

entry	substrate (amt, g)[a]	Ni-Gr2, g	time, h	temp, °C	% conv[b]	product (yield, %)[c]
1	 (2.14) **1**	0.80	18	45	100[d]	 (26) +  (68)
2	**1** (2.56)	1.30	8	120	100	 (95)
3	 (1.84) **2**	0.48	20	50	97[e]	 (85) +  (8) **5** **6**
4	**2** (1.82)	0.49	6	80	100	**5** (59, 78[f]) + **6** (32, 17[f])
5	**2** (1.80)	0.62	16	130	100	**5** (5) + **6** (60)[g] +  (28)[g]
6	 (3.80)	0.70	15	50	98	 (81)
7	 (3.84) **3**	0.71	7	50	80[h]	 (18)[g] +  (30)[g] +  (42)[g] **7** **8** **9**
8	**3** (3.85)	0.68	7	65	100	**7** (79)[g] + **8** (7)[g] + **9** (5)[g]
9	 (3.68) **4**	1.02	22	90	92	 (51)
10	**4** (3.75)	0.95	18	120	100[i]	 (55)

[a] All the reactions were carried out in methanol (50 mL). [b] Conversions were evaluated by GC. [c] Yields refer to pure isolated compounds and are corrected for the unreacted substrate. [d] No hydrogenation took place after 16 h at 30 °C. [e] No hydrogenation occurred after 15 h at 50 °C under 5 atm of hydrogen and after 24 h at 25 °C under 30 atm of hydrogen. [f] The catalyst was previously used for the hydrogenation of 1-decyne (Table III, entry 1). [g] Yields were evaluated by GC. [h] No hydrogenation occurred after 15 h at 25 °C under 30 atm of hydrogen. [i] The hydrogenation was carried out under 50 atm of hydrogen.

at 90 °C, whereas at 120 °C the diol is formed (entries 9 and 10, Table IV). Partial hydrogenolysis or deacylation accounts for the low yields of ketol and diol.[8]

In order to test the catalyst performance after a single operation, we carried out the hydrogenation of α-ionone with the same catalyst previously used for 1-decyne (Table III, entry 1) and observed an improved selectivity as well as an almost unchanged activity (entry 4).

Conclusions

Ni-Gr2 is a less active catalyst than Ni-Gr1, so a higher hydrogen pressure is necessary to achieve semihydrogenation of alkynes, with the stereospecificity being generally lower. However, this drawback is balanced by the large-scale availability and excellent stability on storage (i.e., aging is a severe limitation to the use of Raney nickel).

As a consequence of the reduced activity, Ni-Gr2 displays a good selectivity in the reduction of polyfunctional compounds, i.e., unsaturated carbonyl compounds and β-diketones. Furthermore, it is interesting to note that Ni-Gr2 can be reused with no significative loss of activity. All these factors concur to indicate Ni-Gr2 as a valuable synthetic tool in organic chemistry.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were measured with a Perkin-Elmer R12B instrument (60 MHz) using tetramethylsilane as the internal standard and chemical shifts are reported as δ values. Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrophotometer, and the absorptions are given in reciprocal centimeters. Mass spectra were taken on a Varian MAT 111 instrument at an ionization voltage of 70 eV. Analytical gas chromatography (GC) was performed on a Perkin-Elmer Sigma 3 apparatus equipped with a flame-ionization detector and using 0.25 in. × 6 ft columns (A, 2.5% SE-30 on silanized Chromosorb G, 80–100 mesh; B, 5% FFAP on silanized Chromosorb G, 80–100 mesh; C, 15% Carbowax 20M on Chromosorb W, 80–100 mesh) with a nitrogen flow of 40 mL/min. Peak areas and relative retention times (RRT) were evaluated with the aid of a Perkin-Elmer Sigma 10 Data Station instrument. Thin-layer chromatography was performed on silica gel sheets (Baker 1B2-F). Column chromatography was performed by using Merck silica gel (70–230 mesh). Melting points and boiling points are uncorrected.

Materials. Graphite powder was supplied by Roth, and methanol (Carlo Erba RPE ACS) was used without further purification, whereas tetrahydrofuran (THF) was purified by spinning-band distillation with a Perkin-Elmer 251 Auto Annular Still apparatus. The following commercial substrates were used

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(8) Extensive hydrogenolysis has been observed in the hydrogenation of highly enolizable compounds, i.e., β-diketones: Rylander, P. N.; Steele, D. R. *Engelhard Ind. Tech. Bull.* **1965**, *5*, 113. Moreover, heating (at 100–120 °C) β-diketones in the presence of Raney nickel afforded as byproducts deacylated ketones: Uehara, K.; Ito, M.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1566.

as received: 1-octene, 2-octene (isomer mixture), 2-undecanone, diphenylacetylene (Merck-Schuchardt); ethyl (*E*)-phenylpropenoate, 6-methyl-2,4-heptanedione (Carlo Erba); 1-decyne, phenylacetonitrile, (*R*)-carvone, 1-hexyn-3-ol (Fluka); ethyl 3-phenylpropynoate, 1-methoxy-4-nitrobenzene (Aldrich). Citral (Aldrich), α-ionone, and β-ionone (Fluka) were purified by spinning-band distillation. 5-Decyne and 5-docecyn-7-ol were prepared according to ref 1. 1,1-Diethoxy-3-octyne was synthetized as follows: 1-hexyne (40 mmol) was added to a solution of *n*-butyllithium (2 M in hexane, 40 mmol) in THF (50 mL) at 0 °C in 30 min, and the mixture was stirred for 5 h; after addition of hexamethylphosphoric triamide (6 mL), the solution was treated with 1,1-diethoxy-2-bromoethane (40 mmol) and stirred overnight at room temperature. After aqueous quenching of the reaction, extraction with ether, and distillation, the title compound was recovered in 71% yield: bp 50 °C (1 mm); IR (neat) 1120, 1060; NMR (CCl_4) 4.5 (t, 1 H), 3.5 (m, 4 H), 2.35 (m, 2 H), 2.1 (m, 2 H), 1.4 (m, 4 H), 1.15 (t, 6 H), 0.9 (t, 3 H).

Catalyst Preparation. A flamed, 250-mL, two-necked, round-bottomed flask equipped with an argon inlet and magnetic stirring bar was charged with graphite (10 g) and heated with an oil bath at 160 °C for 30 min under a positive argon pressure. Potassium (3.9 g, 100 mmol) was then added in small, freshly cleaned pieces during 10 min. After the potassium melted, the mixture was vigorously stirred, and the heating was stopped. Potassium–graphite (C_8K)[9] so prepared is a homogeneous bronze powder, which being pyrophoric has to be handled under an inert atmosphere. C_8K was covered with THF (90 mL), and a solution of $NiBr_2\cdot 2DME$ in THF–HMPTA[1] (0.51 M, 98 mL) was added dropwise with stirring during 90 min and cooling with an external bath at 25 °C. Stirring was continued for 5 h, and water (10 mL) was added to destroy any unreacted C_8K. Sequential operations were henceforth carried out with complete air exposure. The solvent was filtered off, and the solid was washed with boiling water (500 mL), methanol (100 mL), and ether (100 mL) and finally dried under vacuum (0.01 mm) for 3 h at 100 °C.

The collected liquid phases contained 98 mmol of bromide ion, while a drop of solution, made ammoniacal, afforded a negative test with dimethylglyoxime. Microanalysis of a sample of Ni-Gr2 gave carbon (69.5%), ash (21%), and minor amounts of hydrogen (1.8%) and nitrogen (0.73%), these last being due to residual HMPTA and water. The nickel content in Ni-Gr2 was 15% as determined, after refluxing a sample (0.5 g) for 1 h with a mixture $HCl-HNO_3$ (3/1, 2 mL), by direct titration with EDTA.

Hydrogenation Apparatus. All the reactions were carried out in a stainless-steel autoclave (vessel volume 1 L, internal diameter 100 mm) equipped with a gas inlet, gas outlet, pressure gauge, glandless magnetically stirrer (200 RPM), electric heater, and temperature control device.

Hydrogenation Reactions. General Procedure. The above-described apparatus was charged with the substrate dissolved in CH_3OH or THF (when the solvent was THF, 1–2% of water was always added since in anhydrous THF hydrogenation rates were considerably lower) and the catalyst and successively purged by being evacuated and filled with hydrogen (four cycles). The autoclave was filled with hydrogen at 30 atm (initial pressure at room temperature), stirred at the required temperature for the times quoted in the tables, and finally cooled to room temperature. After hydrogen removal, the catalyst was filtered off, the solvent was distilled, and products were purified by distillation or column chromatography.

Analysis of Hydrogenation Mixtures. Products derived from hydrogenation of 1-hexyn-3-ol, 1-decyne, 5-decyne, 5-dodecyn-7-ol, diphenylacetylene, and ethyl phenylpropynoate were identified as described in the preceding paper.[1]

Hydrogenation of 1,1-Diethoxy-3-octyne: GC (C, 130 °C) 1,1-diethoxyoctane (10%; RRT 0.43; identical with a sample obtained by acid-catalyzed acetalization of octanal), 1.1-diethoxy-3-octene [79%; RRT 0.52; IR (neat) 1120, 1060, 1010; NMR (CCl_4) 5.35 (m, 2 H), 4.4 (t, 1 H), 3.15–3.8 (m, 4 H), 1.8–2.4 (m, 4 H), 0.8–1.5 (m, 13 H); mass spectrum, *m/e* 157 ($M^+ - C_2H_5O$)], starting alkyne (5%; RRT 1.00).

The *Z/E* ratio of isomeric olefins was determined through stereospecific epoxidation of a sample (0.15 g) with 3-chloroperbenzoic acid (0.15 g) in anhydrous dichloromethane (8 mL) at 0 °C for 4 h. GC analysis (C, 170 °C) revealed a quantitative conversion to the diastereoisomeric epoxides (cis epoxide, RRT 1.00; trans epoxide, RRT 0.88): IR (neat) 1230, 1130, 1060; NMR (CCl_4) 4.55 (t, 1 H), 3.25–3.8 (m, 4 H), 2.6 (m, 2 H), 1.7 (m, 2 H), 0.8–1.55 (m, 15 H). The trans epoxide was unambiguously identified by the enhancing of the GC peak with an authentic sample obtained by reduction of 1,1-diethoxy-3-octyne with a 10-fold excess of sodium in ammonia followed by epoxidation of the resulting (*E*)-alkene (IR 960 cm^{-1}) under the same conditions above reported.

1-Octene: GC (B, 60 °C) octane (96%; RRT 0.81); bp 126 °C; mass spectrum, *m/e* 114 (M^+), identical with a commercial sample. Under the same GC conditions 1-octene has RRT 1.00.

2-Octene: GC (B, 60 °C) octane (95%; RRT 1.00). Under the same GC conditions (*E*)-2-octene has RRT 1.42 and (*Z*)-2-octene RRT 1.52.

Ethyl 3-Phenylpropenoate. Vacuum distillation afforded ethyl 3-phenylpropanoate: 83%; bp 122 °C (14 mm); IR (neat) 1735, 1450, 1370, 1180, 1040, 750, 700; NMR (CCl_4) 7.1 (s, 5 H), 4.0 (q, J = 7 Hz, 2 H), 2.3–3 (m, 4 H), 1.15 (t, J = 7 Hz, 3 H); mass spectrum, *m/e* 178 (M^+).

1-Methoxy-4-nitrobenzene. Starting material (35%) and 1-methoxy-4-aminobenzene [62%; mp 57 °C; IR (melt) 3450, 3370, 3230, 1630, 1520, 1495, 1240, 1090, 820, 720; NMR ($CDCl_3$) 6.65 (m, 4 H), 3.7 (s, 3 H), 3.35 (s, 2 H, NH_2); mass spectrum, *m/e* 123 (M^+)] were separated by column chromatography with hexane–ether (8:2) as eluant.

2-Undecanone. Starting ketone (34%) and 2-undecanol [73%; bp 125 °C (15 mm); IR (neat) 3330, 1460, 1385, 1280, 1115, 720; NMR ($CDCl_3$) 3.7 (m, 1 H), 2.15 (s, 1 H, OH), 1.1–1.6 (m, 19 H), 0.9 (t, 3 H); mass spectrum, *m/e* 172 (M^+, traces), 154 ($M^+ - H_2O$)] were separated by column chromatography, eluting respectively with hexane and with hexane–ether (95/5).

1-Phenyl-1-propanone. Vacuum distillation afforded 1-phenyl-1-propanol: (98%; bp 107 °C (15 mm); IR (neat) 3390, 1450, 1010, 970, 750, 700; NMR ($CDCl_3$) 7.15 (s, 5 H), 4.3 (t, 1 H), 3.75 (s, 1 H, OH), 1.5 (m, 2 H), 0.85 (t, 3 H); mass spectrum, *m/e* 136 (M^+), 118, ($M^+ - H_2O$).

Phenylacetonitrile. Bis(β-phenylethyl)amine [11%; mp 27 °C; IR (melt) 3330, 3050, 1600, 1490, 1450, 1120, 750, 700; NMR ($CDCl_3$) 7.1 (s, 10 H), 2.7 (m, 8 H), 1.05 (s, 1 H, NH); mass spectrum; *m/e* 225 (M^+, traces), 134 ($M^+ - C_7H_7$)] and β-phenylethylamine [71%; bp 198 °C; IR (neat) 3390, 3280, 3080, 3030, 1600, 1490, 1450, 1070, 1030, 740, 700; NMR ($CDCl_3$) 7.15 (s, 5 H), 2.75 (m, 4 H), 1.15 (s, 2 H, NH_2); mass spectrum, *m/e* 121 (M^+)] were separated by column chromatography, eluting respectively with ether and ether/methanol (9/1).

Citral (Table IV, Entry 1). 3,7-Dimethyl-6-octen-1-al [26%; bp 88 °C (13 mm); IR (neat) 2710, 1720, 1450, 1380; NMR (CCl_4) 9.7 (m, 1 H), 5.05 (m, 1 H), 2.2 (m, 2 H), 2.0 (m, 2 H), 1.65 (s, 3 H), 1.55 (s, 3 H), 1.15–1.5 (m, 3 H), 0.9 (m, 3 H); mass spectrum, *m/e* 154 (M^+)] and 3,7-dimethyl-6-octen-1-ol [68%; bp 116 °C (15 mm); IR (neat) 3320, 1450, 1380, 1055; NMR ($CDCl_3$) 5.0 (m, 1 H), 3.55 (t, 2 H), 3.3 (s, 1 H, OH), 2.0 (m, 2 H), 1.65 (s, 3 H), 1.55 (s, 3 H), 1.1–1.5 (m, 5 H), 0.9 (m, 3 H); mass spectrum, *m/e* 156 (M^+, traces), 138 ($M^+ - H_2O$)] were separated by column chromatography, eluting respectively with 98/2 hexane–ether and 9/1 hexane–ether mixtures.

Entry 2. 3,7-Dimethyloctan-1-ol (95%) was purified by distillation: bp 109 °C (16 mm) [lit.[10] bp 102 °C (10 mm)]; IR (neat) 3320, 1460, 1380, 1370, 1050, 1010; NMR ($CDCl_3$) 4.2 (s, 1 H, OH), 3.6 (t, 2 H), 1.1–1.8 (m, 10 H), 0.9 (d, 9 H); mass spectrum, *m/e* 140 ($M^+ - H_2O$), 112 ($M^+ - CH_2CH_2OH$).

α-Ionone (Entry 3). Column chromatography gave two fractions eluted respectively with 97/3 hexane–ether and 9/1 hexane–ether. GC analysis of the former (A, 170 °C) showed 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-one [82%; RRT 0.81; bp 118 °C (15 mm) [lit.[11] bp 120 °C (18 mm)]; IR (neat) 1720,

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1360, 1240, 1160, 1040; NMR (CCl_4) 5.4 (m, 1 H), 2.4 (m, 2 H), 2.0 (s, 3 H), 1.75–1.95 (m, 3 H), 1.65 (m, 3 H), 1.2–1.6 (m, 4 H), 0.9 (s, 3 H), 0.85 (s, 3 H); mass spectrum, *m/e* 194 (M^+)] and α-ionone: 3%; RRT 1.00. The second fraction consisted of 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-ol: 8%; bp 138 °C (18 mm) [lit.[12] bp 130–132 °C (13 mm)]; IR (neat) 3350, 1460, 1130, 1080, 980, 950, 820, 740; NMR ($CDCl_3$) 5.3 (m, 1 H), 3.75 (m, 1 H), 2.3 (s, 1 H, OH), 1.8–2.2 (m, 3 H), 1.7 (m, 3 H), 1.25–1.6 (m, 6 H), 1.15 (d, $J = 6$ Hz, 3 H), 0.94 (s, 3 H), 0.88 (s, 3 H); mass spectrum, *m/e* 196 (M^+).

Entry 5. Column chromatography gave two fractions eluted respectively with 97/3 hexane–ether and 9/1 hexane–ether. The former contained 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-one (5%). GC analysis of the latter fraction (A, 130 °C) revealed the presence of 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)butan-2-ol (60%; RRT 0.93) and of 4-(2,6,6-trimethylcyclohex-1-yl)butan-2-ol: 28%; RRT 1.00; bp 130 °C (13 mm) [lit.[13] bp 90 °C (0.2 mm)]; IR (neat) 3350, 1460, 1380, 1130, 1080; NMR ($CDCl_3$) 3.7 (m, 1 H), 2.4 (s, 1 H, OH), 1.1–1.5 (m, 12 H), 1.15 (d, 3 H), 0.9 (m, 9 H); mass spectrum, *m/e* 180 ($M^+ - H_2O$).

β-Ionone (Entry 6). GC (A, 175 °C) analysis showed 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)butan-2-one [79%; RRT 0.89; bp 126 °C (20 mm) [lit.[11] bp 125 °C (18 mm)]; IR (neat) 1720, 1360, 1160; NMR (CCl_4) 2.3 (m, 2 H), 2.05 (s, 3 H), 1.55 (s, 3 H), 1.3–2.1 (8 H), 1.0 (s, 6 H); mass spectrum, *m/e* 194 (M^+)] and β-ionone: 2%; RRT 1.00.

(*R*)-Carvone (Entry 7). The product distribution was established through GC analysis (B, 140 °C) of five fractions obtained by spinning-band distillation of the crude hydrogenated mixture in the temperature range 101–108 °C (20 mm). Three fractions contained single components with a 75–85% purity. 2-Methyl-5-(1-methylethyl)cyclohexanone: 14%; RRT 0.50; bp 101–102 °C (20 mm); IR (neat) 1715, 1450, 1370, 1320, 1220; NMR (CCl_4) 2.0–2.5 (m, 3 H), 1.3–1.9 (m, 6 H), 0.7–1.05 (m, 9 H); mass spectrum, *m/e* 154 (M^+), 111 ($M^+ - C_3H_7$). 2-Methyl-5-(1-methylethenyl)cyclohexanone: 24%; two peaks, corresponding to epimers at C_2 (RRT 0.61 and 0.66 and area ratio of 55/45); bp 104–105 °C (20 mm); IR (neat) 3090, 1715, 895; NMR (CCl_4) 4.7 (m, 2 H), 2.35 (m, 3 H), 1.3–2.1 (5 H), 1.7 (s, 3 H), 0.95 (m, 3 H); mass spectrum, *m/e* 152 (M^+), 95 ($M^+ - C_4H_9$). 2-Methyl-5-(1-methylethyl)-2-cyclohexen-1-one: 34%; RRT 0.81; bp 106–107 °C (20 mm) [lit.[14] bp 100–102 °C (14 mm)]; IR (neat) 3040, 1675, 1450, 1430, 800; NMR (CCl_4) 6.75 (m, 1 H), 2–2.6 (m, 4 H), 1.3–2.0 (5 H), 0.95 (t, 6 H); mass spectrum, *m/e* 152 (M^+), 82 ($M^+ - C_5H_8$). Starting ketone: 20%; RRT 1.00.

6-Methyl-2,4-heptanedione (Entry 9). Starting dione (8%) and 6-methyl-2-hydroxy-4-heptanone [47%; bp 99 °C (20 mm) [lit.[15] bp 90 °C (12 mm)]; IR (neat) 3430, 1715, 1460, 1405, 1370, 1120, 1030, 940; NMR ($CDCl_3$) 4.15 (m, 1 H), 3.5 (s, 1 H, OH), 2.5 (d, 2 H), 2.25 (m, 2 H), 1.0–1.3 (m, 1 H), 1.15 (d, 3 H), 0.9 (d, 6 H); mass spectrum, *m/e* 144 (M^+), 129 ($M^+ - CH_3$), 126 ($M^+ - H_2O$)] were separated by column chromatography (hexane–ether, 9/1). GC analysis (B, 140 °C) of the fraction containing the ketol revealed the presence of a second component (3% on the basis of area ratio, RRT 1.15) probably due to the isomeric 6-methyl-4-hydroxy-2-heptanone.

Entry 10. Vacuum distillation afforded 6-methyl-2,4-heptanediol: 55%; bp 118 °C (20 mm); IR (neat) 3340, 1460, 1360, 1150, 1120; NMR ($CDCl_3$) 4.5 (s, 2 H, OH), 3.95 (m, 2 H), 0.95–2.0 (5 H), 1.2 (d, 3 H), 0.9 (d, 6 H); mass spectrum, *m/e* 128 ($M^+ - H_2O$), 89 ($M^+ - C_4H_9$).

Registry No. 1, 5392-40-5; **2**, 24190-29-2; **3**, 7059-50-9; **4**, 3002-23-1; **5**, 39721-65-8; **6**, 13720-37-1; **7**, 59471-80-6; **8** (isomer 1), 6909-25-7; **8** (isomer 2), 5524-05-0; **9**, 33375-08-5; 1,1-diethoxy-3-octyne, 79328-69-1; 1-hexyne, 693-02-7; 1,1-diethoxy-2-bromoethane, 2032-35-1; 1,1-diethoxyoctane, 54889-48-4; (*E*)-1,1-diethoxy-3-octene, 79328-70-4; (*Z*)-1,1-diethoxy-3-octene, 79328-71-5; 3,7-dimethyl-6-octen-1-ol, 106-22-9; 3,7-dimethyloctan-1-ol, 106-21-8; 4-(2,6,6-trimethylcyclohex-1-yl)butan-2-ol, 3293-47-8; β-ionone, 14901-07-6; 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)butan-2-one, 17283-81-7; 6-methyl-2-hydroxy-4-heptanone, 59357-17-4; 6-methyl-4-hydroxy-2-heptanone, 57548-36-4; 6-methyl-2,4-heptanediol, 79356-95-9; 1-hexyn-3-ol, 105-31-7; 1-hexen-3-ol, 4798-44-1; 3-hexanol, 623-37-0; 5-decyne, 1942-46-7; decane, 124-18-5; (*Z*)-5-decene, 7433-78-5; (*E*)-5-decene, 7433-56-9; 5-dodecyn-7-ol, 74835-62-4; 6-dodecanol, 6836-38-0; (*Z*)-5-dodecen-7-ol, 79313-71-6; (*E*)-5-dodecen-7-ol, 79313-72-7; diphenylacetylene, 501-65-5; 1,2-diphenylethane, 103-29-7; (*Z*)-1,2-diphenylethene, 645-49-8; (*E*)-1,2-diphenylethene, 103-30-0; ethyl phenylpropynoate, 2216-94-6; ethyl 3-phenylpropanoate, 2021-28-5; ethyl (*Z*)-3-phenylpropenoate, 4610-69-9; ethyl (*E*)-3-phenylpropenoate, 4192-77-2; 1-decyne, 764-93-2; 1-decene, 872-05-9; 1-octene, 111-66-0; octane, 111-65-9; (*E*)-2-octene, 13389-42-9; (*Z*)-2-octene, 7642-04-8; 1-methoxy-4-nitrobenzene, 100-17-4; 1-methoxy-4-aminobenzene, 104-94-9; 2-undecanone, 112-12-9; 2-undecanol, 1653-30-1; 1-phenyl-1-propanone, 93-55-0; 1-phenyl-1-propanol, 93-54-9; phenylacetonitrile, 140-29-4; β-phenylethylamine, 64-04-0; bis(β-phenylethyl)amine, 6308-98-1; 3,7-dimethyl-6-octen-1-al, 106-23-0; Ni, 7440-02-0.

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Preparation and Properties of (2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl Chloride and (2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl Enol Ethers

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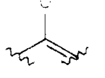
(2,4,6-Tri-*tert*-butylphenoxy)dimethylsilyl chloride (TPS chloride, **3**) is an inexpensive and readily prepared silylating agent for ketones. A variety of silyl enol ethers **4** were obtained by reaction of **3** with ketones. The acid- and base-catalyzed rates of hydrolysis of **4** were examined and compared to the rates for the corresponding trimethylsilyl and *tert*-butyldimethylsilyl enol ethers.

Since House first described a general synthesis of trimethylsilyl enol ethers **1** from trimethylchlorosilane and ketones,[1] these compounds have been shown to be useful enolate equivalents for the synthesis of enones,[2] α-hydroxy



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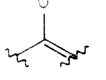

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