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h, and then cooled to room temperature followed by addition of water (1 mL), 3 N aqueous NaOH (2 mL), and 33% aqueous H_2O_2 (2 mL). After having been stirred an additional hour at room temperature, the mixture was separated. The aqueous layer was extracted with hexane (3 × 2 mL). The organic extracts were washed with brine (2 mL) and dried over $K_2CO_3/MgSO_4$. The product, *cis*-5-methylbicyclo[4.3.0]nonan-1-ol (**19a**) (0.03 g, 0.18 mmol) 66% was isolated by flash chromatography (10% EtOAc in hexane on neutral activity III alumina) and found to be identical with the *cis*-5-methylbicyclo[4.3.0]nonan-1-ol (**19a**) prepared via the cyclization of 2-(3-iodopropyl)-2-methylcyclohexanone (**18a**).

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Registry No. **1a**, 83587-99-9; **1b**, 83587-93-3; **1c**, 83588-00-5; **1d**, 93494-17-8; **1e**, 76402-75-0; **1f**, 101493-08-7; **2a**, 52318-93-1; **2b**, 13366-92-2; **2c**, 27935-18-8; **2e**, 3574-58-1; **2f**, 27935-20-2; **3b**, 13366-91-1; **3c**, 27935-17-7; **3e**, 1654-87-1; **3f**, 27935-19-9; **4**, 101493-09-8; **5**, 101517-30-0; **6**, 69007-51-8; **7**, 101493-10-1; **8**, 83587-33-1; **9**, 83587-34-2; **10**, 101493-11-2; **11**, 83587-95-5; **12**, 101517-31-1; **13**, 101493-12-3; **14**, 101493-13-4; **15**, 83587-96-6; **16**, 83587-97-7; **17**, 83587-98-8; **18a**, 101493-14-5; **18b**, 101493-16-7; **18c**, 101493-17-8; **18d**, 101493-19-0; **19a**, 101493-15-6; **19b**, 5173-74-0; **19c**, 101493-18-9; **19d**, 101493-20-3; **20a**, 101493-21-4; **20b**, 101493-23-6; **20c**, 101493-24-7; **20d**, 101493-26-9; **21a**, 101493-22-5; **21c**, 101493-25-8; **21d**, 101493-27-0; **22a**, 101493-28-1; **22a** (tosylate), 101493-33-8; **22c**, 101493-29-2; **22d**, 101493-31-6; **23a**, 101517-32-2; **23c**, 101493-30-5; **23d**, 101493-32-7; ,MeC(OMe)=CH_2, 116-11-0; SmI_2, 32248-43-4.

Liquid-Phase Regioselective 1,4-Hydrogenation of Benzylidene Ketones on Rh/AlPO$_4$ Catalysts

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The liquid-phase catalytic hydrogenation of α,β-unsaturated carbonyl compounds, in the p-$XC_6H_4CH{=}CHCOR$ form (*E* isomers; X = H, Me, MeO, Cl; R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu, *n*-Pe, Ph) was carried out by using a rhodium catalyst supported at 1 wt % on $AlPO_4$ in methanol solvent under low hydrogen pressure (0.55 MPa) at room temperature (298 K). The reactions were found to be highly selective toward the formation of the conjugate reduction product (p-$XC_6H_4CH_2CH_2COR$). In no cases could any appreciable amount of allylic or saturated alcohol be detected, although a small amount of benzyl ketone is obtained in the *p*-chlorobenzylidene ketones due to the hydrogenolysis of the C–Cl bond. The influence of the substituents on the reaction rate is analyzed, and both resonance and steric effects of the COR and R groups, respectively, seem to simultaneously influence the reaction process.

Introduction

Chemoselective hydrogenation of activated double bonds, such as α,β-unsaturated carbonyl functions, has been a long-desired synthetic transformation, since this problem is frequently encountered in synthetic schemes. So, the selective reduction of either the double bond or the carbonyl group of α-enones has been investigated by several workers using different catalytic systems.[1-8] However, some of these methods have not always afforded satisfactory results because of a lack of consistent regiospecificity and the fact that some hydride reagents are quite difficult to prepare.

Rhodium catalysts have attracted much attention from the viewpoint of synthetic organic, as well as from that of industrial chemistry, due to their high catalytic activity and easy preparation and reduction.

In this paper the Rh/$AlPO_4$ system[9,10] is described as a new heterogeneous hydrogenation catalyst for the selective liquid-phase reduction, at room temperature, of the carbon–carbon double bond of α-enones of different types and structures. This catalyst is easily prepared and stable on long storage.

The study of the influence of ketone structure on reactivity shows that the functional groups on the carbon–carbon double bond affect the hydrogenation activity by electronic and steric effects, specially the first one.

From the present study seventeen new ketones of the type p-$XC_6H_4CH_2CH_2COR$ are reported. Although a search of the literature revealed that five of these ketones are known, they were reported without physical and spectroscopic properties.

Results and Discussion

Diffusion Control, Reaction Kinetics, and Solvent Effect. Several hydrogenation runs, performed at various agitation regimes and with different amounts of catalyst, showed that the initial rates of hydrogenation were directly

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Table I. Effect of the New Addition of Substrate on the Activity of $Rh/AlPO_4$ for the Hydrogenation of 5 mmol of Benzylideneacetone in 50 mL of Methanol at 298 K, 0.55 MPa, and 300 min^{-1}

hydrogenation run	initial reaction rate $10^4 r_0$ mol min^{-1}
1	3.391
2	3.317
3	3.434
3	3.434
4	3.371
5	3.160

proportional to the catalyst weight and not affected by the shaking regime above 200 min^{-1}. These factors, together with the small particle size of the catalyst, lower than 0.149 nm, excluded the possibility that external and/or internal diffusion limited the rate of hydrogenation.

The hydrogenation rates for all substrates studied were of zero order in the concentration of benzylidene ketone (0.1–3 M) and of first order in initial hydrogen pressure (0.40–0.70 MPa) under conditions where the reaction was kinetically controlled.

So, the bond formation between substrate and metal must precede hydrogen activation, this being the rate determining step, as is generally accepted in these cases.[13-15] Therefore, the effect of the substrate structure on the hydrogenation rate must be interpreted in terms of the stability of the metal–olefin species, according to a Horiuti–Polanyi mechanism modified in agreement with the irreversible adsorption of alkene[16] because of the zero order in substrate concentration.

Thus, to a good approximation, the rate of hydrogenation on $Rh/AlPO_4$ can be seen as simply proportional to the rate at which hydrogen strikes the sites available to it. Accordingly, the kinetic equation for the systems under study can be written as

$$r = dC/dt = kP_{H_2} \quad (1)$$

where k is the reaction rate constant and P_{H_2} is the initial hydrogen pressure.

On the other hand, as the hydrogenation proceeded it was observed that after about 50–60% conversion the reaction rate gradually diminished. Explanations based on poisoning and catalyst deactivation could be ruled out because of the following observation: the catalyst preserved almost 100% initial activity for another batch of substrate ($PhCH{=}CHCOCH_3$) after the first sample had been completely converted into the saturated ketone. The same was observed with a third, fourth, or fifth new addition of substrate as is evident from the data given in Table I. This behavior is similar to observations made during the liquid–phase hydrogenation of linear and cyclic alkenes[9,17,18] and functionalized alkenes[10,19,20] on $Ni/AlPO_4$ and $Rh/AlPO_4$ catalysts. This reaction rate decrease can be rationalized by the change of the reaction orders with respect to the substrate from zero to first because at very low concentrations the catalyst surface is "starved" of olefin molecules. Thus, our work is only concerned with the linear portion of the plot of the hydrogen pressure decrease vs. reaction time, where the reaction rate is zero order with respect to the substrate concentration.

Solvents play an important role on the heterogeneous catalytic hydrogenation as has been previously reported.[10,21-23] Thus, preliminary experiments performed with different alcohols as solvents, showed that the highest reaction rates were obtained with methanol due to its higher dielectric constant. Thus, it was used for the hydrogenations here described.

Because the reaction rate increases with the dielectric constant of alcoholic solvents, it can be concluded that the process takes place through intermediates with some polar characteristics or that the solvent influences bond energies of the activated complex during the surface reaction, the latter being the more probable effect.

This behavior is similar to that observed in liquid-phase hydrogenation of alkenes and functionalized alkenes over $Ni/AlPO_4$, $Ni/AlPO_4$–SiO_2, and $Ni/AlPO_4$–Al_2O_3 catalysts[22] as well as over $Rh/AlPO_4$ and $Rh/AlPO_4$–SiO_2 catalysts.[10,23]

However the solvent effect on the rate and selectivity of catalytic hydrogenation needed a complex approach to the reaction systems because the study of any particular effect, regardless of other effects, leads to an exaggerated simplification, and the individual results cannot be applied to other systems. Thus, the generalization of results is feasible only by assuming a complex view (multiparameter equations) of the reaction systems, because all the operative effects in the process are related to each other.[24]

Hydrogenation Reaction Rates and Hydrogenation Reaction Products. To evaluate the hydrogenation activity of the 1 wt % $Rh/AlPO_4$ catalyst, the initial rates of hydrogenation, r_0, were obtained from a least-squares fit to the slopes of initially linear hydrogen-decrease vs. reaction-time curves. The results for all substrates studied, based on at least three repeated measurements of the hydrogenation run, are collected in Table II.

In all cases, the conjugate reduction products were obtained with complete selectivity, and no unsaturated or saturated alcohols were detected. Only small amounts of benzyl ketones were obtained when *p*-chlorobenzylidene ketones were hydrogenated, but never higher than 7 wt % of the hydrogenation product.

In some independent runs carried out to test reproducibility, the hydrogen adsorption rate varied about 6–8%, but no changes in conversion or chemoselectivity were observed. Moreover, variations in initial rates for samples derived from independent impregnations and/or initial reduction of the $Rh/AlPO_4$ catalyst were not observed either. Thus, $Rh/AlPO_4$ is a very promising catalyst for selective hydrogenation of carbon–carbon double bonds since it may be used with little loss of activity and reactions may be carried out easily and rapidly.

As can be seen, the reaction is sensitive to the substituents on the carbonyl group, indicating a 1,4-adsorption state with subsequent isomerization of enol. Moreover, a decrease in rate was noted when sterically hindered α,β-unsaturated ketones were hydrogenated. This again suggests that the adsorption of the substrate on the metal surface takes place prior to hydrogen activation, and can be interpreted in terms of the stability and reactivity of metal–olefin species.[13]

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Table II. Hydrogenation of Benzylidene Ketones over Rh/AlPO$_4$ (1 wt %)[a]

4-XC_6H_4CH=CHCOR		initial rate[b] 10^6r_o/mol s^{-1}	areal rate[c] 10^6r_a/mol $s^{-1}m^{-2}_{RH}$	4-XCH_2CH_2COR		
X	R			R_f[d]	IR[e] ν_C=O, cm^{-1}	mol[f] formula
H	Me	5.65	0.314	0.603	1715	$C_{10}H_{12}O$
H	Et	4.77	0.265	0.646	1710	$C_{11}H_{14}O$
H	*n*-Pr	3.95	0.220	0.646	1710	$C_{12}H_{16}O$
H	*i*-Pr	3.96	0.220	0.646	1708	$C_{12}H_{16}O$
H	*n*-Bu	4.79	0.266	0.664	1710	$C_{13}H_{18}O$
H	*t*-Bu	2.06	0.114	0.690	1700	$C_{13}H_{18}O$
H	*n*-Pe	3.58	0.199	0.768	1710	$C_{14}H_{20}O$
H	Ph	7.17	0.108	0.744	1682	$C_{15}H_{14}O$
Cl	Me	6.59	0.403	0.637	1715	$C_{10}H_{11}ClO$
Cl	Et	6.34	0.375	0.692	1710	$C_{11}H_{13}ClO$
Cl	*n*-Pr	6.21	0.364	0.692	1705	$C_{12}H_{15}ClO$
Cl	*i*-Pr	6.53	0.351	0.708	1700	$C_{12}H_{15}ClO$
Cl	*n*-Bu	4.57	0.358	0.733	1700	$C_{13}H_{17}ClO$
Cl	*t*-Bu[g]	6.28	0.270	0.730	1700	$C_{13}H_{17}ClO$
Cl	*n*-Pe	2.11	0.295	0.739	1705	$C_{14}H_{19}ClO$
Cl	Ph	2.13	0.118	0.741	1672	$C_{15}H_{13}ClO$
MeO	Me	5.69	0.316	0.608	1705	$C_{11}H_{14}O_2$
MeO	Et	5.15	0.286	0.576	1705	$C_{12}H_{16}O_2$
MeO	*n*-Pr[h]	4.24	0.236	0.653	1705	$C_{13}H_{18}O_2$
MeO	*i*-Pr	4.30	0.339	0.640	1700	$C_{13}H_{18}O_2$
MeO	*n*-Bu[h]	4.34	0.241	0.672	1705	$C_{14}H_{20}O_2$
MeO	*t*-Bu	3.33	0.185	0.678	1700	$C_{14}H_{20}O_2$
MeO	*n*-Pe[h]	3.71	0.206	0.500	1705	$C_{15}H_{22}O_2$
MeO	Ph	2.08	0.115	0.661	1682	$C_{16}H_{16}O_2$
Me	Me	7.26	0.398	0.746	1715	$C_{11}H_{14}O$
Me	Et	6.75	0.366	0.735	1710	$C_{12}H_{16}O$
Me	*n*-Pr	6.56	0.352	0.698	1705	$C_{13}H_{18}O$
Me	*i*-Pr	6.31	0.345	0.707	1705	$C_{13}H_{18}O$
Me	*n*-Bu	6.45	0.363	0.701	1710	$C_{14}H_{20}O$
Me	*t*-Bu[i]	4.87	0.254	0.709	1700	$C_{14}H_{20}O$
Me	*n*-Pe	5.32	0.349	0.726	1705	$C_{15}H_{22}O$
Me	Ph	2.13	0.117	0.727	1690	$C_{16}H_{16}O$

[a] Operating conditions: 50 mL of 1 M methanolic solution of benzylidene ketone over 0.2 g of catalyst at 25 °C, 0.55 MPa and 300 min^{-1}. [b] From the initial linear hydrogen decrease vs. reaction time curves, and based on three repetitive measurements (6–8% error). [c] Initial rate per unit of surface area of supported rhodium (S_{Rh} = 90 m^2 g$^{-1}_{Rh}$). [d] TLC Aluminum sheets, silica gel 60 PF$_{254}$-Merck and CHCl$_3$ as eluent. [e] KBr pellets or NaCl plates. [f] The microanalysis of the purified compounds show the following maximum deviations from the calculated values: C ± 0.42; H ± 0.20; Cl ± 0.12. [g] Reported as patent (Balasubramanyan, S.; Shephard, M.; Batch, J. J.; Boize, L. M. Ger. Offen. 2737489, 1978; *Chem. Abstr.* **1978**, *88*, P184647n). [h] Reported without spectroscopic properties (Alba, A.; Aramendia, M. A.; Borau, V.; Garcia-Raso, A.; Jimenez, C.; Marinas, J. M. *Can. J. Chem.* **1984**, *62*, 917). [i] Reported as patent (Holmwood, G.; Heinz, K. H.; Luerssen, K.; Frohberger, P. E.; Brandes, W. Eur. Pat. Appl. EP 40345, 1982; *Chem. Abstr.* **1982**, *96*, P104256m).

On the other hand, the initial rate obtained for the hydrogenation of benzylidenacetone is lower than that previously found for the hydrogenation of 3-penten-2-one. This may be adscribed to the electron cloud of the conjugated aromatic system interfering with the ability of the olefinic bond to sit on the catalyst surface, together with steric effects of the aromatic ring.

A search of the literature revealed that twelve of the saturated ketones are here for first time. Moreover, although five of these ketones are know (two as patents), they were previously reported without spectroscopic properties.

The elemental analyses and infrared carbonyl stretching frecuencies for all ketones are collected in Table II; the boiling points and ^{1}H NMR spectral data of undescribed *p*-substituted benzylidene ketones are reported as supplementary material (see paragraph of the end of paper about supplementary material).

Table III. Reaction Constants, ρ_H and δ_X, and Regression Coefficients, R_T, of the Plot log k/k_0 vs. ρ_H and E_S (X Substituent)

R	ρ_H	δ_X	R_T
Me	0.08	−0.10	0.987
Et	0.03	−0.13	0.990
n-Pr	0.24	−0.21	0.990
i-Pr	0.20	−0.19	0.985
n-Bu	0.33	−0.13	0.999
t-Bu	−0.10	−0.31	0.991
n-Pe	0.15	−0.14	0.958
Ph	−0.03	−0.03	0.995

Effect of the Nature of X and R on the Hydrogenation Rate of the Carbon–Carbon Double Bond in *p*-XC_6H_4CH=CHCOR (*E* Isomers) Compounds. The influence of structure on reactivity is a topic of current interest in the study of the mechanism of alkene hydrogenation on supported metal catalysts. Thus, different authors have studied this problem in order to find out how the polar or steric effects of the substituent affect the adsorptivity of the unsaturated compounds or the reactivity of the adsorbed species.[25]

a. **Nature of X.** Because of its para position the X group should have no steric effect on the reaction rate, but might have an electronic one. However, the results in Table II show that there is no clear relationship between the electronic properties of the X group and the hydrogenation rate.

Since the determination of the influence that substituents exert on the rate of a reaction is usually discussed within the context of the linear free-energy relationship (LFER), the Hammett, Taft, and Pavelich-Taft equations[26-28] being the most popular examples in organic chemistry, we have examined these equations for several parameters taken from the literature[29-32] such as σ_p, σ_R, σ_H, σ_S, σ_I, E_S, etc.

On testing the Hammett equation with the σ-parameters mentioned above, we have not obtained good linear correlations in any case although in the case of the σ_H, a substituent constant accounting for the enthalpic contribution,[30,31] only a reasonably good fit was obtained. When we tested the Taft equation with the relative reaction rates and the steric factors of the X groups,[29] good fits were obtained with regression coeficients above 0.9. The rate data were fitted to the Pavelich–Taft equation in an attempt to correlate relative reactivities with enthalpic (σ_H) and steric (E_S) constants. A reasonably good fit was obtained for the equation

$$\log(k/k_0) = \rho_H\sigma_H + \delta_X E_S \qquad (2)$$

where k_0 is the reaction rate for X = Me, k is the rate for the X group, σ_H and E_S are the substituent parameters which are characteristic for the enthalpic and steric effects, respectively, and ρ_H and δ_X the corresponding reaction constants.

The results shown in Table III were obtained by least-squares multiple regression.

Other planar regressions obtained by combining σ-parameters ($\sigma_I - \sigma_R$ and $\sigma_S - \sigma_H$) or $\sigma - E_S$ parameters were not successful.

Thus, the major role of the X group is of an enthalpic and steric nature modifying the adsorption strength be-

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Table IV. Reactions Constants, ρ_R and δ_R, and Regression Coefficients, R_T, of the Plot $\log k/k_0$ vs. $\rho_R - E_S$ (R Substituent)

X	ρ_R	δ_R	R_T
H	3.26	0.12	0.999
Me	1.45	0.04	0.999
MeO	4.83	0.11	0.992
Cl	1.70	0.04	0.999

tween the substrate and the catalyst surface and, thereby, the hydrogenation rate.

The results reported in Table III show that in all cases investigated the δ_X constant which measures the susceptibility of the reaction to the steric effects, has a negative value, i.e., the reaction rate seemed to be helped by bulky substituents in the para position of the aromatic ring.

On the other hand the contribution of enthalpy to the substituent effect provides a clear indication of the relative importance of resonance effects, since resonance-interacting substituents were found to be enthapy-controlled and the resonance interactions are only important for electron-donating groups.[30,31] The resonance contribution decreases for bulky R groups, indicating the importance of the R group steric effect on the hydrogenation rate as indicated below. The results obtained reveal the major contribution of enthalpy to the changes in the standard free energy of the reaction.

b. Nature of R. As shown in Table II, R plays an important role in the hydrogenation rate. These functional groups can affect the olefinic bond hydrogenation by electronic and/or steric effects modifying the electronic density of the carbon–carbon double bond or blocking the reaction centre. In addition, the reaction process may be modified by competitive adsorption of the COR functional group on catalyst-active sites.

In a previous letter[20] on the hydrogenation of substrates in the form PhCH=CHCOR (*E* isomers; R = Me, Et, *i*-Pr, *t*-Bu, Ph, OMe, OH) with the same Rh/$AlPO_4$ catalyst used here, we obtained the best correlation with σ_R (resonance contribution) for the COR group although a good degree of correlation was also obtained for the steric parameter, E_S, of the R group. So, both conjugative and steric effects seem to influence the reaction process by simultaneous action.

The introduction of Me, MeO, and Cl groups in 4-position in benzylidene ketones seems not to modify this observation. Thus, for branched alkyl R substituents (*i*-Pr, *t*-Bu) the initial rate, in all cases, decreased in the same order, indicating the importance of the steric effects on the hydrogenation rate. For linear alkyl substituents (methyl to pentyl) the initial hydrogenation rate decreased with the length of the hydrocarbon chain, especially for the *n*-pentyl derivative. This fact seems to indicate a predominance of the steric effect over the +I electron donor ability of R.

Thus, we have examined jointly both electronic and steric effects by applying the Pavelich-Taft equation (28)

$$\log (k/k_0) = \rho_R\sigma_R + \delta_R E_S \qquad (3)$$

where K_0 is the reaction rate for R = Me, k is the rate for the R group, σ_R is the resonance contribution of the COR group, E_S is the steric parameter of the R group, and ρ_R and δ_R are the corresponding reaction constants.

The results summarized in Table IV were obtained by least-squares multiple regression. As can be seen, the main influence on the reaction rate is the resonance contribution of the COR group with a positive value of the ρ_R constant. On the other hand, the δ_R constant, which measures the susceptibility of the reaction to steric effects, has in all cases a positive value, so that the reaction rate is decreased by bulky substituents.

Thus, the influence of the structure of benzylidene ketone on its hydrogenation activity can be accounted for by taking into consideration both the resonance and steric effects of the X and R groups acting jointly in the reaction process. Both resonance effects increased the reaction rate while the steric ones displayed opposite effects, i.e., the reaction rate was helped by δ_X and inhibited by δ_R.

Conclusions

The hydrogenation of benzylidene ketones over Rh/$AlPO_4$ catalysts is influenced by the simultaneous action of both conjugative and steric effects of the X and R groups. Rh/$AlPO_4$ is found to be a very efficient heterogeneous catalyst for the regioselective 1,4-hydrogenation of α,β-unsaturated ketones into the corresponding saturated ones. This fact, together with its ability to hydrogenate the carbon–carbon double bond of a variety of functionalized alkenes,[19] its inactivity toward hydrogenolysis in propargyl derivatives and toward double bond isomerization, and the facile workup consisting in a safe filtration of the nonpyrophoric solid phase, shows its utility as a hydrogenation catalyst. Its use for preparative-scale hydrogenation in organic synthesis is highly recommended, except for unsaturated substrates with an aldehyde function, where strong adsorption of the aldehyde group on the catalyst surface makes the substrate act as a catalyst poison.

Experimental Section

General Methods. Infrared spectra were obtained on a Perkin-Elmer 599A spectrophotometer. ^1H NMR spectra were obtained on a Varian Associates EM-390 (90 MHz) instrument. They are reported in δ units using Me_4Si as the internal standard. Mass spectra were recorded on a Hewlett-Packard 5992B instrument. GLC analyses were performed on a Hewlett-Packard 5711 instrument equipped with a column packed with 10% U.C. on Chromosorb W 60/80. Peak areas were measured by a Hewlett-Packard 3880A electronic digital integrator. TLC was carried out on aluminum plates coated with silica gel (Merck, Kieselgel 60 PF_{254}) using $CHCl_3$. Melting points were determined on an oil bath melt apparatus and were not corrected. Elemental analyses were determined by the Organic Chemistry Institute (CSIC) Laboratories. Solutions in organic solvents were dried with anhydrous magnesium sulfate. Solvents were evaporated on a Büchi rotary evaporator.

Materials. All benzylidene ketones (*E* configuration) were prepared through Claisen–Schmidt condensation by reacting the corresponding aldehydes with several methyl alkyl ketones using activated barium hydroxide as the catalyst according to a procedure previously described.[11] They are purified by either distillation or recrystallization before use, and the purity was verified by GLC and ^1H NMR.

Methanol, used as the hydrogenation solvent, was of spectroscopic grade and used without further purification.

Preparation and Storage of Catalysts. Activated barium hydroxide was prepared by calcination of $Ba(OH)_2{\cdot}8H_2O$ (Merck) for 3 h at 200 °C. It was activated at 140 °C for 1 h before use. % Ba^{2+}: 70.2 wt. The catalyst may be stored in a desiccator over NaOH for several days without appreciable loss of activity.

The aluminum orthophosphate used as the rhodium support was obtained by precipitation with propylene oxide from aqueous solutions of $AlCl_3{\cdot}6H_2O$ and H_3PO_4 (85 wt %). The solid thus obtained was washed with isopropyl alcohol, dried at 120 °C for 24 h and then calcined at 650 °C for 3 h in an electric muffle furnace and stored in a desiccator, S_{BET}: 228 $m^2\,g^{-1}$.[12]

The rhodium-supported $AlPO_4$ catalyst was prepared by impregnation of aluminum orthophosphate with an aqueous solution of $RhCl_3{\cdot}3H_2O$ (Merck, p.a.) to yield a nominal 1 wt % Rh, using the incipient wetness method. The slurry was stirred for 24 h, then the water was evaporated on a rotary vacuum evaporator and the solid was dried at 120 °C for 24 h. The impregnated support was reduced in flowing hydrogen (100 mL min^{-1}, 99.999%, $H_2O < 3$ ppm) at 200 °C for 7 min and then cooled to room temperature maintaining the same hydrogen stream. The $AlPO_4$-supported rhodium catalyst thus prepared has a metal surface area of 90 $m^2g^{-1}{}_{Rh}$[9,10].

Hydrogenation Apparatus and General Procedure. All experiments were conducted with a Parr Instruments 3911 hydrogenator at an initial hydrogen pressure of 0.55 MPa and at 25 °C. The temperature was controlled by pumping water from a thermostatic bath through the vessel jacket with a precision of 0.5 °C.

The compound to be reduced (5 mmol) and methanol (50 mL) were placed in the hydrogenation vessel (250 mL) and then the catalyst (200 mg) was added. The vessel was connected to the hydrogenator, twice flushed with hydrogen, pressurized to 0.55 MPa. and shaken until absorption of 1 equiv of hydrogen. The progress of hydrogenation was then followed by recording the hydrogen uptake vs. time, at constant volume. Catalytic activity is determined as the initial rate of hydrogenation, from the slope of the linear hydrogen pressure decrease vs. reaction time, remaining linear up to 50–60% conversion.

After filtration and elimination of methanol by rotary vacuum evaporation, the hydrogenation products were purified by crystallization or silica column chromatography and, in the case of the compounds previously described, were identified by comparison of their spectroscopic properties (^1H NMR and IR spectra) with those described in the literature.

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Registry No. (*E*)-$PhCH{=}CHCOMe$, 1896-62-4; (*E*)-$PhCH{=}CHCOEt$, 18402-88-5; (*E*)-$PhCH{=}CHCOPr$-*n*, 8297-62-9; (*E*)-$PhCH{=}CHCOPr$-*i*, 10596-48-2; (*E*)-$PhCH{=}CHCOBu$-*n*, 41903-83-7; (*E*)-$PhCH{=}CHCOBu$-*t*, 29569-91-3; (*E*)-$PhCH{=}CHCOPe$-*n*, 29478-39-5; (*E*)-$PhCH{=}CHCOPh$, 614-47-1; (*E*)-4-$ClC_6H_4CH{=}CHCOMe$, 30626-03-0; (*E*)-4-$ClC_6H_4CH{=}CHCOEt$, 54951-47-2; (*E*)-4-$ClC_6H_4CH{=}CHCOPr$-*n*, 100765-36-4; (*E*)-4-$ClC_6H_4CH{=}CHCOPr$-*i*, 67962-15-6; (*E*)-4-$ClC_6H_4CH{=}CHCOBu$-*n*, 100765-37-5; (*E*)-4-$ClC_6H_4CH{=}CHCOBu$-*t*, 41564-62-9; (*E*)-4-$ClC_6H_4CH{=}CHCOPe$-*n*, 100765-38-6; (*E*)-4-$ClC_6H_4CH{=}CHCOPh$, 22252-16-0; (*E*)-4-$MeOC_6H_4CH{=}CHCOMe$, 3815-30-3; (*E*)-4-$MeOC_6H_4CH{=}CHCOEt$, 82297-64-1; (*E*)-4-$MeOC_6H_4CH{=}CHCOPr$-*n*, 82297-65-2; (*E*)-4-$MeOC_6H_4CH{=}CHCOPr$-*i*, 67962-14-5; (*E*)-4-$MeOC_6H_4CH{=}CHCOBu$-*n*, 82297-66-3; (*E*)-4-$MeOC_6H_4CH{=}CHCOBu$-*t*, 41564-61-8; (*E*)-4-$MeOC_6H_4CH{=}CHCOPe$-*n*, 82297-67-4; (*E*)-4-$MeOC_6H_4CH{=}CHCOPh$, 22252-15-9; (*E*)-4-$MeC_6H_4CH{=}CHCOMe$, 4023-84-1; (*E*)-4-$MeC_6H_4CHCHCOEt$, 81467-93-8; (*E*)-4-$MeC_6H_4CH{=}CHCOPr$-*n*, 100765-39-7; (*E*)-4-$MeC_6H_4CH{=}CHCOPr$-*i*, 67962-11-2; (*E*)-4-$MeC_6H_4CH{=}CHCOBu$-*n*, 100765-40-0; (*E*)-4-$MeC_6H_4CH{=}CHCOBu$-*t*, 41564-60-7; (*E*)-4-$MeC_6H_4CH{=}CHCOPe$-*n*, 100765-41-1; (*E*)-4-$MeC_6H_4CH{=}CHCOPh$, 22252-14-8; $Ph(CH_2)_2COMe$, 2550-26-7; $Ph(CH_2)_2COEt$, 20795-51-1; $Ph(CH_2)_2COPr$-*n*, 29898-25-7; $Ph(CH_2)_2COPr$-*i*, 40463-09-0; $Ph(CH_2)_2COBu$-*n*, 19969-04-1; $Ph(CH_2)_2COBu$-*t*, 5195-24-4; $Ph(CH_2)_2COPe$-*n*, 6047-99-0; $Ph(CH_2)_2COPh$, 1083-30-3; 4-$ClC_6H_4(CH_2)_2COMe$, 3506-75-0; 4-$ClC_6H_4(CH_2)_2COEt$, 95416-62-9; 4-$ClC_6H_4(CH_2)_2COPr$-*n*, 54672-63-8; 4-$ClC_6H_4(CH_2)_2COPr$-*i*, 100765-42-2; 4-$ClC_6H_4(CH_2)_2COBu$-*n*, 100765-43-3; 4-$ClC_6H_4(CH_2)_2COBu$-*t*, 66346-01-8; 4-$ClC_6H_4(CH_2)_2COPe$-*n*, 100765-44-4; 4-$ClC_6H_4(CH_2)_2COPh$, 5739-39-9; 4-$MeOC_6H_4(CH_2)_2COMe$, 104-20-1; 4-$MeOC_6H_4(CH_2)_2COEt$, 5440-80-2; 4-$MeOC_6H_4(CH_2)_2COPr$-*n*, 90831-80-4; 4-$MeOC_6H_4(CH_2)_2COPr$-*i*, 100765-45-5; 4-$MeOC_6H_4(CH_2)_2COBu$-*n*, 90831-81-5; 4-$MeOC_6H_4(CH_2)_2COBu$-*t*, 100789-95-5; 4-$MeOC_6H_4(CH_2)_2COPe$-*n*, 90831-82-6; 4-$MeOC_6H_4(CH_2)_2COPh$, 1669-49-4; 4-$MeC_6H_4(CH_2)_2COMe$, 7774-79-0; 4-$MeC_6H_4(CH_2)_2COEt$, 100765-46-6; 4-$MeC_6H_4(CH_2)_2COPr$-*n*, 100765-47-7; 4-$MeC_6H_4(CH_2)_2COPr$-*i*, 100765-48-8; 4-$MeC_6H_4(CH_2)_2COBu$-*n*, 100765-49-9; 4-$MeC_6H_4(CH_2)_2COBu$-*t*, 80917-20-0; 4-$MeC_6H_4(CH_2)_2COPe$-*n*, 100765-50-2; 4-$MeC_6H_4(CH_2)_2COPh$, 1669-50-7.

Supplementary Material Available: Boiling points and full ^1H NMR data of compounds **10–15**, **19–23**, and **26–31** (2 pages). Ordering information is given on any current masthead page.

Alkylated Perepoxides: Peroxonium vs. Phenonium Intermediates from β-Haloalkyl *tert*-Butyl Peroxides and Silver Trifluoroacetate

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To see if the generation of cyclic peroxonium ions by intramolecular alkylation of dialkyl peroxides could be extended to 3- or 4-membered ring systems, seven β-iodoalkyl *tert*-butyl peroxides were treated with silver trifluoroacetate in refluxing dichloromethane. Compounds **1a–d**, $RCH_2C(Me)(OOBu$-*t*$)CH_2I$ (R = H, Me, Et, or Ph), gave mixtures of 1,2-peroxy-migrated substitution and elimination products $RCH_2C(Me)(OCOCF_3)$-CH_2OOBu-*t*, $CH_2{=}C(CH_2R)CH_2OOBu$-*t*, and $RCH{=}C(Me)CH_2OOBu$-*t*, whereas compounds **1e–g**, $PhC(R)$-$(OOBu$-*t*$)CH_2I$ (R = H, Me, or Ph), afforded 1,2-phenyl-migrated products. The results were rationalized in terms of the selective generation of intermediate alkylated perepoxides from **1a–d** or phenonium ions from **1e–g**. The relative migratory aptitudes were found to be Ph > Bu-*t*-OO > alkyl.

Perepoxides have been postulated as intermediates in the singlet oxygenation of alkenes[1] and in the reaction of β-hydroperoxy bromides with base,[2] but their existence remains a matter of controversy. In continuing our investigations on the generation of peroxonium ions by intramolecular alkylation of dialkyl peroxides,[3-5] we have obtained evidence that species closely related to perepoxides, the hitherto unknown alkylated perepoxides, me-

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