tentatively identified. One high-boiling compound, which gave the final GC peak, could not be identified. A few additional products of very minor importance (e.g., RCOCH=CHR) were observed by CI.

The formation of the reaction products can be most readily explained by the assumption that R· can abstract hydrogen from the ring and that it can also induce a ring-opening of cyclopropane[17] (see Scheme I). The formation of tri- and tetrasubstituted propanes in the presence of a large excess of cyclopropane indicates that hydrogen atom abstraction from $RCH_2CH_2CH_2R$ is faster than the attack of R· on cyclopropane. Multisubstitution that involves an intermediate RC species is clearly in competition with a β-scission process which yields the O=C moiety and the CF_3NCF_3 radical. This last-named radical is presumed to be the precursor of $CF_3N=CF_2$, which, in reaction(s) with R·, yields of $CF_3N=C=O$.

Kinetic data on the reaction are summarized in Table II. In the absence of cyclopropane there was no measurable decay of R· over 5×10^6 s. In the presence of cyclopropane, decay occurred with clean first-order kinetics over many half-lives.[20] The measured half-lives were independent of the initial concentration of R· which rules out any kinetic role for R_2. They were also independent of whether the reaction was carried out in the dark or in daylight, which rules out any kinetic role by an excited state of R· (λ_{max} 545 nm, ϵ_{max} 4.44 in CCl_4).[21] The half-lives were, however, inversely proportional to the cyclopropane concentration.

The true bimolecular rate constant, k_x, for the initial attack of R· on cyclopropane was obtained by dividing the experimentally measured first-order rate constant, k_{expt}, by twice the molar concentration of cyclopropane; i.e., $k_x = k_{expt}/2[C_3H_6]$, the factor of 2 arising because the carbon-centered radical formed initially is rapidly trapped by a second R·. The ratio of the rate of the initial substitution to form the $RCH_2CH_2CH_2$· radical to the rate for H-atom abstraction to form the cyclopropyl radical; i.e., k_S/k_A, can be very roughly estimated (provided the unidentified material is ignored) from the product yield ratio, $\sum$[substituted propanes]/[substituted cyclopropane], to be ca. 4:1. Taking k_x to be 6×10^{-8} M^{-1} s^{-1} (see Table II) yields $k_s \approx 4.8 \times 10^{-8}$ M^{-1} s^{-1} and $k_A \approx 1.2 \times 10^{-8}$ M^{-1} s^{-1} at room temperature.

In summary, the reaction of the pseudohalogen, $(CF_3)_2NO$·, with cyclopropane at room temperature occurs mainly (ca. 80%) by a slow, but kinetically simple bimolecular homolytic substitution at carbon. We presume that

halogen atoms induce ring-opening by a similar process.

Experimental Section

Product Studies. Cyclopropane and R· (30:1 mole ratio) were condensed at 77 K into EPR tubes and were sealed under vacuum. On warming to room temperature, a homogeneous liquid phase was obtained, and, after 3 months at room temperature, the aminooxyl had been completely consumed. Tubes were cooled to −80 °C and opened, and a 5–10-fold excess by volume of a hydrocarbon diluent (isopentane, isooctane, or isopropylbenzene) that had also been cooled to −80 °C was added and thoroughly mixed with the reaction products and unreacted cyclopropane. A sample for analysis was withdrawn by using a precooled (−80 °C) microsyringe; only one sample was analyzed from each tube. This procedure reduced the loss of volatile materials to a minimum, and essentially identical results were obtained in duplicate runs.

The reaction products were analyzed by GC/MS on an HP 5992 instrument using EI and on an HP 5985 instrument using CI with methane. Products were separated on a 12 ft × $^1/_8$ in. stainless steel column packed with 12% OV 101 on Chromosorb W (high performance). The chromatograph was run isothermally at 50 °C for 10 min, and the temperature was then raised at a rate of 10 °C/min to 200 °C. The helium flow rate was 18 mL/min, and the injection port and detector temperatures were 150 and 200 °C, respectively. The GC trace obtained by EI MS is available as supplementary material, as are the computer printouts of the EI MS of the principal peaks in the chromotogram. The supplementary material also contains a summary of the CI MS, for which only values of $m/z \geq 100$ were measured.

Kinetic Studies. Reaction samples, prepared in EPR tubes by high-vacuum techniques, contained known concentrations of R· in neat cyclopropane or in cyclopropane/Freon 11 ($CFCl_3$) mixtures having known concentrations of cyclopropane. The concentrations of R· were such that no significant concentrations of the dimer known to form at low temperatures[22] were present at the reaction temperature of 295 ± 2 K. The decay of R· was monitored by standard methods.

Supplementary Material Available: Tables III–XIV giving mass spectral data for reaction products (11 pages). Ordering information is given on any current masthead page.

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(17) We recognize that product identification solely by GC/MS can never be 100% definitive. Nevertheless, we are confident that one product is the R· + cyclopropyl radical adduct and that many of the other products are derived from a ring-opened cyclopropane. A potential alternative route to the latter compounds[18] which involves the intermediacy of an allyl radical formed by the ring-opening of an initially produced cyclopropyl radical can, we believe, be unequivocally ruled out. The cyclopropyl to allyl radical rearrangement is extremely slow,[19] while R· (like other aminooxyls) will react with carbon-centered radicals at, or near, the diffusion-controlled limit. At the low temperatures and high R· concentrations of our experiments, it is inconceivable that cyclopropyl ring-opening could occur in competition with its trapping by R·.

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Gas–Liquid Phase-Transfer Catalysis: Catalytic and Continuous Transesterification Reaction

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Phase-transfer catalysis (PTC)[1] implies two main phenomena: the first is the anion transfer from the liquid or solid phase to the organic one where the reaction takes place, and the second is the anion activation that is due to the absence of strong interactions between the transferred anion and its environment.

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Table I. Transesterification of Ethyl Acetate with Several Alcohols under GL-PTC Conditions[a]

	catalytic bed[b] effect on % conversion[c]		
alcohol	K_2CO_3	K_2CO + 5% Carbowax 6000	K_2CO_3 + 5% 18-crown-6
methanol		54, 34[d]	31[e]
n-propanol		33	
n-butanol		42, 34[d]	17[e]
isobutanol		46	
sec-butyl alcohol		2	
tert-butyl alcohol		traces	
1-pentanol	36	53	61

[a] Temperature = 170 °C; flow rate (liquid), 60 mL/h; ester/alcohol molar ratio, 1:2. [b] 400 g. [c] Conversions were established by GLC analysis, comparing ethyl acetate and the produced alkyl acetate after calibration with authentic samples. [d] 180 g of catalytic bed. [e] 30 g of catalytic bed.
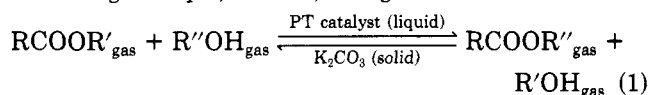
Table II. Transesterification of n-Amyl Acetate under GL-PTC Conditions with Several Alcohols on 400 g of Catalytic Bed Composed of K_3CO_3 + 5% Carbowax 6000[a]

alcohol	% conversion[b]	alcohol	% conversion[b]
methanol	91	n-propanol	65
ethanol	75	n-butanol	58

[a] Temperature = 170 °C; flow rate (liquid), 60 mL/h; ester/alcohol molar ratio, 1:2. [b] Conversions were established by GLC analysis, comparing n-amyl acetate and the produced alkyl acetate after calibration with authentic samples.

Transesterification reactions[2] are carried out in the presence of a catalytic amount of acid or base, which respectively activate the leaving alcohol or the entering alkoxide group; the reaction between an ester and an alcohol, if carried out in the presence of a phase-transfer catalyst, therefore necessarily implies the activation of the alcohol through formation of the active alkoxide anion. This equilibrium reaction has not yet been reported under solid–liquid phase-transfer catalysis conditions; furthermore, complete hydrolysis of the esters occurs in the alkaline aqueous medium required for liquid–liquid phase-transfer catalysis conditions.

We here report some transesterification reactions carried out under gas–liquid phase-transfer (GL-PTC) conditions,[3] according to eq 1; that is, the gaseous mixture of the

$$RCOOR'_{gas} + R''OH_{gas} \underset{K_2CO_3 \text{ (solid)}}{\overset{PT \text{ catalyst (liquid)}}{\rightleftharpoons}} RCOOR''_{gas} + R'OH_{gas} \quad (1)$$

reactant ester and alcohol is allowed to pass continuously through solid potassium carbonate coated with a phase-transfer (PT) catalyst and contained in a glass column. The exchange products are collected by cooling at the column outlet.

The results reported in Tables I–III illustrate the reaction of ethyl acetate, n-pentyl acetate, and methyl benzoate, respectively. The reported data are referred to an unvarying composition of the collected mixture, since at the beginning of the reaction the retention times, dif-

Table III. Transesterification of Methyl Benzoate under GL-PTC Conditions with Several Alcohols[a]

	catalytic bed[b] effect on % conversion[c]			
alcohol	K_2CO_3	K_2CO_3 + 5% Carbowax 6000	K_2CO_3 + 5% 18-crown-6	TsOH on silica gel[d]
ethanol		24		
n-propanol		12		
n-butanol	1	23, 12[e]	36	0
1-pentanol		65	34	
1-octanol		21		

[a] Temperature = 170 °C; flow rate (liquid), 60 mL/h; ester/alcohol molar ratio, 1:2; pressure, 20 torr. [b] 400 g. [c] Conversions were established by GLC analysis, comparing methyl benzoate and the produced alkyl benzoate after calibration with authentic samples. [d] p-Toluenesulfonic acid, 3% by weight on silica gel coated with 5% Carbowax 6000; 100 g of bed. [e] 200 g of bed.

ferent for the different products, produce a reaction mixture richer in the more volatile compounds, as occurs in gas chromatographic processes.

The bed remains active for an indefinite period: the same catalytic bed was used for all the reactions, after removing the compound left over from the previous reaction by heating the column under vacuum. Tests of the bed activity, carried out by repeating some of the reactions reported, yielded reproducible results.

When the amount of catalytic bed is increased, the reagent contact time increases and, consequently, the conversion produced. For the moment, however, we cannot be sure whether the reaction mixture obtained with the larger column (400 g of bed) reached the composition corresponding to the thermodynamic equilibrium of the four involved compounds. Adsorption phenomena make the relative concentrations of the four compounds in the liquid phase of the molten catalyst different from those in the gas phase. Since GL-PTC catalyzed reaction is carried out in an open system, an equilibrium mixture different from that of the thermodynamic equilibrium may result.

No reaction takes place under the reported conditions when the solid bed is composed by an acidic catalyst (toluenesulfonic acid adsorbed on silica gel, Table III), and, moreover, the potassium carbonate alone is not able to promote the reaction to an appreciable extent, as previously reported for the synthesis of phenyl esters and sulfides under GL-PTC conditions.[4] The phase-transfer catalyst, which constitutes the liquid film widely dispersed over the solid potassium carbonate, promotes the reaction by complexing and transferring the salt into the organic phase where the carbonate anion is activated.[5] In attaining this, 18-crown-6 was more active than the linear polyether Carbowax 6000. The anion activation of the carbonate produces, via exchange, the alkoxide anion that is in equilibrium with the alcohol. The steady-state concentration of the alkoxide is very low; in fact, the reaction between ethyl bromide and ethanol gave only traces of ethyl ether under the here-reported conditions even with 18-crown-6 as a catalyst.

The anion activation also results from the data on reactivity reported in Table I, where CH_3OH > primary ≫

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(5) As in some liquid–liquid phase-transfer catalyzed reactions in the presence of strong bases (Makosza, M. *Pure Appl. Chem.* **1975**, *43*, 439–462), complete transfer of the carbonate ion into the organic phase is not really necessary. The exchange reaction may occur between the base and ROH diffusing into the liquid film at the K_2CO_3 (solid)–catalyst(liquid) interface.

secondary > tertiary alcohol. This reactivity trend follows the relative basicity order of the respective alkoxide anions.

Steric hindrance of reagents and adsorption of the heavier compounds on the bed are determining factors in the process, and their total effect clearly appears when one compares the data within Tables I and II. Both an increase of molecular dimension of the primary alcohol and the steric hindrance at the carbonyl group of the ester cause a decrease of conversion.[6] However, conversion increases if the starting ester is high boiling, therefore remaining longer on the bed (cf. EtOAc with AmOAc).[7]

The nature of the leaving alkoxide group is also important. Thus, the reaction between *t*-BuOAc and *n*-BuOH over 400 g of K_2CO_3 containing 5% by weight of Carbowax 6000 only yielded 5% of transesterification product, showing that no alkyl scission occurs and that this process is also controlled by the basicity of the leaving group.

The application of GL-PTC to the transesterification reactions allows the reaction to be carried out in a continuous way and in the absence of solvents. On coupling a catalytic and a distillation column, one could produce pure ester and alcohol with the continuous recycling of the not converted compounds. At the end of the process the expensive 18-crown-6 can be easily recovered, extracting the bed in a Soxhlet apparatus with diethyl ether.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Hitachi-Perkin Elmer R-24 60-MHz spectrometer. GLC analyses were performed on a Varian 1400 instrument equipped with a CDS 111L integrator and a column of 5% SE-30 on Varaport. A double-jacketed glass column (750 mL in volume, 60 cm in length) thermostated with a Lauda MGW ultrathermostat and an FMI lab pump, Type RRP, were used. Organic and inorganic reagents were ACS reagent grade.

Preparation of the Catalytic Bed. The catalyst (Carbowax 6000 or 18-crown-6, 5% by weight with respect to the base) was dissolved in methanol, potassium carbonate was added, and the suspension was evaporated to remove the solvent. The solid mass obtained was oven-dried at 130 °C for 3 h.

Typical Procedure of Transesterification under GL-PTC Conditions: Reaction between Ethyl Acetate and 1-Butanol. A 1:2 molar solution of ethyl acetate and 1-butanol (1.0:1.9 v/v) was passed at a flow rate (liquid) of 60 mL/h through the column thermostated at 170 °C and containing 400 g of K_2CO_3 coated with Carbowax 6000 (5% by weight). The cooled reaction mixture was analyzed by GLC (temperature 100 °C) and by ^{1}H NMR. All the products were confirmed by comparison with authentic samples. The conversion reported in Table I (42%) was constant after 25 mL of reagent mixture was passed through the column. No byproduct was detected in any of the cases examined.

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(6) The reaction between ethyl valerianate and *n*-butanol, under the here-reported conditions, yielded only 9% conversion into *n*-butyl valerianate (400 g of bed constituted of K_2CO_3 coated with 18-crown-6, 5% by weight).

(7) When the difference between the boiling points of the leaving alcohol and of the produced ester is great, conversions corresponding or higher than those at the equilibrium point are obtained (Table II and III). This fact, necessarily linked with the partial pressure of the products in the reactor, alows one to foresee that higher or 100% conversions could be reached by a one-step process, controlling the pressure during the reaction.

Active Metals from Potassium–Graphite. Zinc–Graphite-Promoted Synthesis of β-Hydroxy Esters, Homoallylic Alcohols, and α-Methylene-γ-butyrolactones

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Within the area of metal-catalyzed or -promoted organic reactions, an increasing interest is addressed to the use of highly active forms of zerovalent metals.[1] They include thin films, supported or unsupported small particles, blacks, sponges, colloids, and even ligand-stabilized clusters,[2] which represent the boundary between homogeneous and heterogeneous catalysis.

We have recently reported a new method for the preparation of highly reactive metals by the potassium–graphite (C_8K) reduction of the corresponding metal halides (MX_n) in ethereal solvents according to eq 1.[3–6] Nickel-,[4] palla-

$$nC_8K + MX_n \rightarrow C_{8n}M + nKX \qquad (1)$$
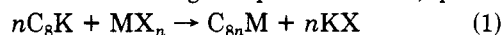
dium-,[5] and iron–graphite[6] obtained by this procedure were found to be useful catalysts or reagents in organic chemistry.

We now report the use of zinc–graphite (Zn–Gr)[7] in the preparation of Reformatsky reagents and allylic zinc bromides.

The Reformatsky reaction,[8] because of its simplicity and the ready availability of the requisite reagents, is still one of the best routes to β-hydroxy esters. Several improvements[9–15] have been reported in recent years to overcome the drawbacks (variable yields, side reactions, etc.) associated with the original Reformatsky reaction.

We have carried out several experiments exploiting Zn–Gr in Reformatsky reactions and in homoallylic alcohols syntheses (Table I). Optimized conditions require the preparation of Zn–Gr in tetrahydrofuran (THF) under argon, followed by addition of the bromo derivative and carbonyl compound at 0 °C in the case of α-bromo esters and at 20 °C in the case of allylic bromides. We believe that the excellent yields obtained, comparable and in some instance superior to those reported by the previously quoted procedures,[9–15] are due to the high activity of Zn–Gr which allows a quantitative formation of organozinc derivative. Side reactions (self-condensation of the α-bromo ester or carbonyl compound and elimination or retro-

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(7) The X-ray diffraction spectrum of a sample of Zn–Gr washed with water suggests a dispersion of zinc on the graphite surface; moreover, weak reflections due to intercalated species are also observed.[3]

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