operating at 100 and 25.15 MHz, respectively. All ^{1}H and ^{13}C shifts are reported relative to Me$_4$Si. Mass spectra were obtained on Hitachi Model RMU-6L and MS 50-A.E.I. mass spectrometers at 70 eV by the direct insertion method.

General Procedure. Appropriate amounts (2, 3.8, and 4.5 mol) of anisole (1) and phenetole (2) were condensed with a fixed (1 mol) amount of dichloroacetyl chloride at room temperature in the presence of 1.5–2 mol of anhydrous AlCl$_3$. The acid chloride was added in portions with continuous shaking to a mixture of anhydrous AlCl$_3$ and either 1 or 2, and the reaction mixture was left for 24 h. The product was decomposed with an ice–HCl mixture and then taken up with ether. The ether solution was washed free from acid and dried under reduced pressure, and the residue was subjected to column chromatography over silica gel followed by crystallization. Thus, 2 mol of 1 and 2 gave rise to 3 and 4, respectively, while 3.8 mol of 1 and 2 led to the formation of 7 and 4, respectively. When 4.5 mol of 1 was employed a mixture of 5 and 7 was liberated whereas a mixture of 6 and 8 was isolated when the same molar quantity of 2 was used.

2,2-Dichloro-1,1-bis(4-methoxyphenyl)ethylene (3). This was eluted with petroleum ether–benzene (95:5), yield 1.7 g from 5.4 g of 1, and crystallized from MeOH: mp 107–108 °C (lit.[12] mp 109 °C); MS, m/z (relative intensity) 310 (M + 2, 64), 308 (M$^+$, 100), 273 (9), 238 (58), 223 (19), 195 (17), 151 (19); ^{1}H NMR δ 3.86 (s, 6 H, C4'-OCH$_3$), 6.89 (d, J = 8 Hz, 4 H, C3'-H, C5'-H), 7.25 (d, J = 8 Hz, 4 H, C2'-H, C6'-H); ^{13}C NMR δ 55.1 (t, C4'-OCH$_3$), 113.5 (d, C3', C5'), 130.7 (d, C2', C6'), 132.0 (s, C1'), 139.7 (s, C1, C2), 159.1 (s, C4').

2,2-Dichloro-1,1-bis(4-ethoxyphenyl)ethylene (4). In column chromatography it was eluted with petroleum ether, yield 1.8 g from 6.1 g of 2: mp 102–103 °C (MeOH) (lit.[12] mp 105 °C); MS, m/z (relative inensity) 338 (M + 2, 29), 336 (M$^+$, 47), 310 (5), 308 (9), 282 (15), 280 (23), 210 (79), 181 (88), 152 (100); ^{1}H NMR δ 1.42 (t, J = 7 Hz, 6 H, C4'-OCH$_2$CH_3), 4.05 (q, J = 7 Hz, 4 H, C4'-OCH_2CH$_3$), 6.84 (d, J = 8 Hz, 4 H, C3'-H, C5'-H), 7.22 (d, J = 8 Hz, 4 H, C2'-H, C6'-H); ^{13}C NMR δ 14.8 (q, C4'-OCH$_2$CH$_3$), 63.4 (t, C4'-OCH$_2$CH$_3$), 114.0 (d C3', C5'), 130.7 (d, C2', C6'), 131.9 (s, C1'), 139.8 (s, C1, C2).

2,2-Dichloro-1,1-bis(4-methoxyphenyl)ethane (5). It was eluted with petroleum ether–benzene (85:15), yield 1.9 g from 13.5 g of 1: mp 116–117 °C (MeOH) (lit.[13] mp 114 °C); MS, m/z (relative intensity) 312 (M + 2,4), 310 (M$^+$, 8), 240 (3), 228 (24), 227 (100), 212 (6), 169 (6), 165 (5), 153 (7), 152 (7), 141 (6), 113 (6); ^{1}H NMR δ 3.81 (s, 6 H, C4'-OCH$_3$), 4.52 (d, J = 8 Hz, 1 H, C1-H), 6.34 (d, J = 8 Hz, 1 H, C2-H), 6.89 (d, J = 8 Hz, 4 H, C3'-H, C5'-H), 7.30 (d, J = 8 Hz, 4 H, C2'-H, C6'-H); ^{13}C NMR δ 55.1 (q, C4-OCH$_3$), 68.9 (d, C1), 75.3 (d, C2), 114.0 (d, C3', C5'), 129.4 (d, C2', C6'), 132.1 (s, C1'), 158.8 (s, C4').

2,2-Dichloro-1,1-bis(4-ethoxyphenyl)ethane (6). Elution with petroleum ether–benzene (90:10) afforded 6, yield 1.5 g from 15 g of 2: mp 72–73 °C (MeOH) (lit.[13] mp 73 °C); MS, m/z (relative intensity) 340 (M + 2, 12), 338 (M$^+$, 18), 303 (56), 268 (5), 255 (100), 226 (5), 197 (6); ^{1}H NMR δ 1.42 (t, J = 7 Hz, 6 H, C4'-OCH$_2$CH_3), 4.02 (q, J = 7 Hz, 4 H, C4'-OCH_2CH$_3$), 4.48 (d, J = 8 Hz, 1 H, C1-H), 6.25 (d, J = 8 Hz, 1 H, C2-H), 6.85 (d, J = 8 Hz, 4 H, C3'-H, C5'-H), 7.24 (d, J = 8 Hz, 4 H, C2'-H, C6'-H); ^{13}C NMR δ 14.9 (q, C4'-OCH$_2$CH_3), 63.3 (t, C4'-OCH_2CH$_3$), 69.0 (d, C1-H), 75.3 (d, C2-H), 114.1 (d, C3', C5'), 129.4 (d, C2', C6'), 132.1 (s, C1'), 158.7 (s, C4').

1,1,2,2-Tetrakis(4-methoxyphenyl)ethylene (7). Petroleum ether–benzene (85:15) eluted 7, yield 2 g from 10 g of 1 (crystallized from MeOH): mp 182–183 °C (lit.[14] mp 183–184 °C); MS, m/z (relative intensity) 452 (M$^+$, 100), 437 (M$^+$ − CH$_3$, 25), 301 (28), 238 (63), 226 (61), 223 (33), 199 (60); ^{1}H NMR δ 3.80 (s, 12 H, C4'-OCH$_3$), 6.68 (d, J = 8 Hz, 8 H, C3'-H, C5'-H), 6.98 (d, J = 8 Hz, 8 H, C2'-H, C6'-H); ^{13}C NMR δ 55.0 (q, C4'-OCH$_3$), 113.0 (d, C3', C5'), 132.5 (d, C2', C6'), 136.8 (s, C1'), 138.3 (s, C1, C2), 157.8 (s, C4').

1,1-Bis(4-ethoxyphenyl)ethylene (8). It was eluted with petroleum ether, yield 2.6 g from 15 g of 2: mp 140 °C (MeOH) (lit.[12] mp 138 °C); MS, m/z (relative intensity) 268 (M$^+$, 90), 253 (M$^+$ − CH$_3$, 12), 240 (25), 239 (32), 211 (75), 197 (85), 182 (45),

180 (65), 164 (100), 152 (71), 151 (75), 138 (50), 114 (61); ^{1}H NMR δ 1.46 (t, J = 7 Hz, 6 H, C4'-OCH$_2$CH_3), 4.04 (q, J = 7 Hz, 4 H, C4'-OCH_2CH$_3$), 5.28 (s, 2 H, C2-H), 6.85 (d, J = 8 Hz, 4 H, C3'-H, C5'-H), 7.24 (d, J = 8 Hz, 4 H, C2'-H, C6'-H); ^{13}C NMR δ 14.9 (q, C4'-OCH$_2$CH$_3$), 63.4 (t, C4'-OCH$_2$CH$_3$), 111.4 (t, C2), 114.0 (d, C3', C5'), 129.3 (d, C2', C6'), 134,2 (s, C1'), 149.0 (s, C1), 158.6 (s, C4').

Kinetics and Mechanism of the Reaction between Phenyl Isocyanate and Alcohols in Benzene Medium

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The reactions between an isocyanate (RNCO) and a variety of alcohols, producing industrially useful urethans, have been studied from the kinetic and the mechanistic points of view by a number of workers.[1-5] For instance, Davis and Farnum[1] found that the order of reactivity of primary, secondary, and tertiary alcohols with phenyl isocynate was approximately 1.0, 0.3, and 0.003–0.007, respectively. Baker and co-workers[2-4] observed this reaction to be base catalyzed. They also observed catalysis by alcohol itself.[2] The title investigation has been undertaken in order to find out if a correlation exists between the structure of alcohols and the kinetic parameters.

Experimental Section

AnalaR benzene, phenyl isocyanate (bp 66–68 °C (25 mm)), and alcohols were purified by standard methods and fractionally distilled, collecting the middle cuts for kinetic measurements.

Kinetic measurements were carried out in a benzene medium at 20, 30, and 40 ± 0.1 °C. Depending upon the reaction rate, [alcohol] was always kept higher (1.5 to 4 times) than [phenylisocyanate]. Kinetics was followed by mixing thermally equilibrated solutions of phenyl isocyanate and alcohol in benzene. Aliquots from the reaction mixture were withdrawn at regular time intervals and poured into a known excess of n-butylamine, and the amine was back-titrated against standard sulfuric acid to methyl red end point.[6] Over the periods normally required for the actual runs, the phenyl isocyanate solutions in benzene were quite stable. The reactions were followed up to 50–70% conversion.

Results and Discussion

The reaction of phenyl isocyanate with various alcohols studied followed second-order kinetics, in accord with the rate expression (1).

$$\frac{-d[C_6H_5NCO]}{dt} = k_2 \, [\text{alcohol}][C_6H_5NCO] \qquad (1)$$

Plots of log $[b(a-x)/a(b-x)]$ against t were linear and

(12) Harris, E. E.; Frankforter, G. B. *J. Am. Chem. Soc.* **1926**, *48*, 3144.
(13) Riemschneider, R. *Monatsh.* **1953**, *84*, 1228.
(14) Buckles, R. E.; Womer, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 5055.

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Table I. Kinetic Parameters for the Reaction between Phenyl Isocyanate and Some Alcohols in Benzene Medium

|	$10^4 k_2$, M^{-1} s^{-1}					$\Delta G^{\ddagger}$,	$-\Delta S^{\ddagger}$,
alcohol	20 °C	30 °C	40 °C	E_a,[a] kcal/mol	log A	kcal/mol	eu (30 °C)
methyl alcohol	1.84	3.08	5.01	9.0 ± 0.12	2.98	22.6	46.9
ethyl alcohol	2.08	3.34	5.37	8.6 ± 0.16	2.71	22.6	48.2
n-propyl alcohol	1.89	3.17	5.13	8.8 ± 0.08	2.84	22.6	47.6
n-butyl alcohol	1.93	3.15	5.13	8.8 ± 0.13	2.84	22.6	47.6
allyl alcohol	0.18	0.35	0.68	12.0 ± 0.17	4.20	23.9	41.3
methoxyethanol	0.12	0.20	0.38	11.4 ± 0.11	3.55	24.3	44.3

[a] E_a values obtained by the method of least squares. [b] Concentration unit, mol/L.

passed through the origin for all the alcohols. The values of k_2 were evaluated from the slopes of these linear plots. For a given alcohol at constant temperataure, the k_2 values were reproducible and the values given in Table I are the average of three runs.

The validity of (1) was further confirmed by the plots of log $b/(b-x)$ against t, which were linear and passed through the origin. The plot of log k'_1 (where k'_1 is the pseudo-first-order rate constant) against log a was linear with a slope of unity, confirming that the reaction is first order in alcohol. That the reaction is first order in C$_6$H$_5$NCO was proved by the linear plot of log $(-d$-[C$_6$H$_5$NCO]/dt) vs. log [C$_6$H$_5$NCO] with a slope of 0.95. For each alcohol the value of the Arrhenius activation energy (Ea), log A, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ are given in Table I.

Baker and co-workers[2] observed that increase in initial [alcohol] increased the rate, and this was assumed to be due to the alcohol itself acting as a catalyst. However, this assumption of Baker and co-workers[2] is not supported by their data. For instance, in benzene medium, for phenyl isocyanate-methyl alcohol reaction[4] at 20 °C with [C$_6$H$_5$NCO] = 0.24 M and [CH$_3$OH] = 0.48 M, the value of $10^4 k_2$ was 2.3 M^{-1} s^{-1}. When [CH$_3$OH] was increased to 2.4 M, the value of $10^4 k_2$ increased only to 3.67 M^{-1} s^{-1}. Under similar conditions, for phenyl isocyanate-ethyl alcohol reaction[4] at 20 °C, the value of $10^4 k_2$ increased from 2.2 to 3.15 M^{-1} s^{-1} only. Evidently the magnitude of increase in the rate constant is very small and cannot be attributed to the catalysis by alcohol itself. Moreover, for both methanol and ethanol, the activation energy was higher at higher [alcohol] as compared to that at lower [alcohol] thereby ruling out catalysis by alcohol. Dyer and co-workers[5] also observed only a small increase in rate for the n-butyl alcohol-phenyl isocyanate reaction in xylene at 25 °C. For example, at [C$_6$H$_5$NCO]/[BuOH] ratios of 1:2 and 1:5, the values of $10^4 k_2$ were 4.38 and 4.88 M^{-1} s^{-1}, respectively. This observation again cannot be considered as an indication of true catalysis by the alcohol. Moreover, an alcohol-catalyzed reaction should be kinetically of the third order, and such an observation has not been made by any of the workers.

In the present work, increasing the [alcohol]/[C$_6$H$_5$NCO] ratio did not show any appreciable increase in the rate constant. For [allyl alcohol]/[C$_6$H$_5$NCO] ratios in the range of 1.5–4.0, the value of $10^4 k_2$ was almost constant (0.18 M^{-1} s^{-1}). When the ratio was increased to 8.0, 10.0, 11.5, and 16.0, some increase in $10^4 k_2$ value was observed but the increase was not significant. (For example, $10^4 k_2$ was 0.27 M^{-1} s^{-1} when the ratio was 16). The increase in rate observed by Baker and co-workers may be

Scheme I

C$_6$H$_5$—N═C═O + ROH ⇌ [C$_6$H$_5$NCO·ROH]

(activated complex)
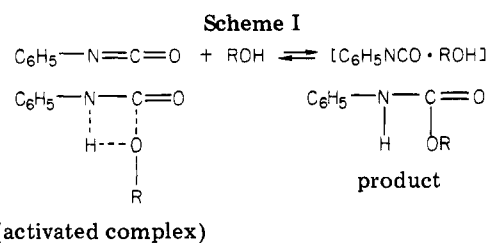
due to the increase in polarity of solvent as a result of increase in [alcohol] beyond a certain limit since alcohols possess a significant dipole moment. Other workers[7,8] have also observed that for dipole–dipole reactions, increasing the concentration of one of the reactants beyond a certain limit enhances the rate and have attributed the effect to the increase created in the polarity of the medium by one of the reactants.

In order to arrive at a plausible mechanism for the reaction between an alcohol and an isocyanate, the best approach would be to treat this reaction as a simple dipole–dipole reaction. Phenyl isocyanate may exist in any one of the following forms, with a net positive charge on
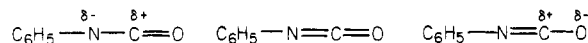
the carbon atom. The primary role of an alcohol is that of an electron donor with the result that the oxygen atom of the alcohol attacks the carbonyl carbon of the isocyanate. The observed overall second-order kinetics is thus explained. However, the formation of a loose alcohol–C$_6$H$_5$NCO complex as a reaction intermediate cannot be altogether ignored.[9,10]

For a second-order reaction taking place in the temperature range (20–40 °C) studied, all the values of the activation energy (Ea) are low and the entropies of activation $\Delta S^{\ddagger}$ are high and negative values. Since no ionic species are involved in the reaction and since $\Delta S^{\ddagger}$ values are high and negative, it is reasonable to conclude that the reaction occurs by a concerted mechanism as shown in Scheme I.

There is the possibility of the alcohol existing as (ROH)$_n$. If the polymer reacts with RNCO in the rate-determining step, cyclic dimer of the type A could be formed, which

A
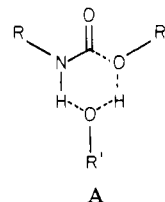
again could account for high negative $\Delta S^{\ddagger}$ values.

(1) Davis, T. L.; Farnum, J. M. *J. Am. Chem. Soc.* **1934**, *56*, 883.
(2) Baker, J. W.; Davies, M. M.; Gaunt, J. *J. Chem. Soc.* **1949**, 24.
(3) Baker, J. W.; Holdsworth, J. B. *J. Chem. Soc.* **1947**, 713.
(4) Baker, J. W.; Gaunt, J. *J. Chem. Soc.* **1949**, 9, 19, 27.
(5) Dyer, E.; Taylor, H. A.; Mason, S. J.; Samson, J. *J. Am. Chem. Soc.* **1949**, *71*, 4106.
(6) Siggia, S.; Hanna, J. G. *Anal. Chem.* **1948**, *20*, 1084.

(7) Seshadri, K. V. Ph.D. Thesis, University of Madras.
(8) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1956**, *78*, 3637.
(9) Banthrope, D. V. *Chem. Rev.* **1970**, *70*, 295.
(10) Subramanian, R. M.; Ganesan, R. *Indian J. Chem., Sect. B* **1977**, *15B*, 645.

It has been shown[11,12] that for dipole–dipole reactions in solution the Arrehenius activation energies give a measure of the electron densities at the reaction centers. The constancy of k_2 and Ea values for the reactions involving methyl, ethyl, n-propyl, and n-butyl alcohols (Table I) indicates that the electron-releasing inductive effect of the alkyl group in these four alcohols has little effect, as expected, on the electron density on the oxygen atom. In contrast to these alcohols, the activation energies for the reactions involving allyl alcohol and methoxyethanol are definitely higher by about 2 kcal mol^{-1}, and this is clearly due to the electron-attracting nature of the allyl and methoxy groups, as a consequence of which the electron density on the oxygen atom is reduced.

The dipole–dipole type of mechanism proposed in Scheme I was further confirmed by the following additional experimental observations. When chloro- or bromo-substituted ethyl alcohol was used as the reactant there was no reaction at 40 °C even after 6 h. The powerful electron-attracting capacity of the halogen atoms diminishes the electron density on the oxygen atom of the alcohol and drastically reduces the rate by increasing the activation energy Ea. The activated complex in the reaction is more polar than the reactants and hence an increase in the polarity of the solvent should increase the rate. It is found to be true since in chlorobenzene (ϵ = 5.6) the reaction proceeds at a faster rate than in benzene (ϵ = 2.2). For the n-butyl alcohol–phenyl isocyanate reaction in chlorobenzene, the value of $10^4 k_2$ was 5.9 M^{-1} s^{-1} at 30 °C and the corresponding Ea value was 7.3 kcal/mol (compare with values in Table I).

(11) Laidler, K. J. "Chemical Kinetics"; McGraw Hill: New York, 1965; p 241.
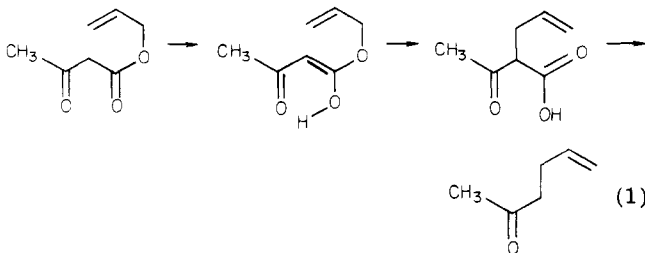(12) Hinshelwood, C. N.; Laidler, K. J.; Timm, E. W. *J. Chem. Soc.* 1938, 848.

The Ester Enolate Carroll Rearrangement

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The Carroll rearrangement[1,2] is an old and well-established thermal rearrangement (eq 1) that involves the re-

arrangement of allylic esters to β-keto acids followed by decarboxylation. The reaction, while in principle a ver-
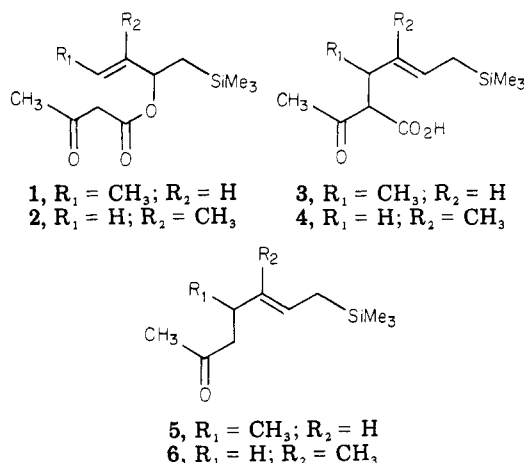
satile complement to the Claisen rearrangement,[3] has not found widespread use. This is probably for two reasons: (1) the lack of a convenient high-yield method for the formation of β-keto esters[4] and (2) the harsh conditions required to effect rearrangement.[5,6]

We report a mild and high-yield synthesis of allylic acetoacetates[7] and conditions for their rearrangement at room temperature or in refluxing THF. Although several reports[8] on the Carroll rearrangement allude to the fact that the reaction seems to be accelerated by base, there has been no specific study of the ester enolate[9] version of this reaction.

We have discovered that dianions[10] of allylic acetoacetates, generated by treatment of the acetoacetates with 2 equiv of LDA at −78 °C in THF, rearrange at room temperature or at reflux and *the resulting β-keto acids can be readily isolated.* For example, acetoacetates 1 and 2

1, R$_1$ = CH$_3$; R$_2$ = H   3, R$_1$ = CH$_3$; R$_2$ = H
2, R$_1$ = H; R$_2$ = CH$_3$ 4, R$_1$ = H; R$_2$ = CH$_3$

5, R$_1$ = CH$_3$; R$_2$ = H
6, R$_1$ = H; R$_2$ = CH$_3$

could be isomerized to β-keto acids 3 and 4 in 84% and 40% yields, respectively.[11] Heating the β-keto acids in CCl$_4$ solution for 1 h at 77 °C leads to decarboxylation. A number of examples are collected in Table I. Where possible the yield and product ratios have been compared to the pyrolysis method.

The acetoacetates used in this study were prepared in high yield by treatment of allylic alcohols[12] in ether at −20 °C with diketene and a catalytic amount of 4-(dimethylamino)pyridine (DMAP)[13] followed by stirring at room temperature. A number of examples are given in Table II. This method represents a significant improvement

(1) Carroll, M. F. *J. Chem. Soc.* 1940, 1226.
(2) Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* 1943, 65, 1992.

(3) Ziegler, F. E., *Acc. Chem. Res.* 1977, 10, 227.
(4) A promising new method involves the reaction of 5-acyl Meldrum's acid with allylic alcohols: Oikawa, Y.; Sugano, K.; Yonemitsu, O. *J. Org. Chem.* 1978, 43, 2087.
(5) Rearrangement is normally carried out at temperatures of 130–220 °C by heating the β-keto ester neat or in a high-boiling solvent (xylene, diphenyl ether), usually after in situ preparation of the β-keto ester.
(6) An interesting report of the low-temperature Pd(0)-catalyzed rearrangement of allylic β-keto esters has appeared: Shimizu, I.; Yamada, T.; Tsuji, J. *Tetrahedron Lett.* 1980, 21, 3199.
(7) Acetoacetic esters of other types of alcohols have been prepared by this procedure.
(8) Bases include the following. (a) Al(i-PrO)$_3$: Cookson, R. C.; Parsons, D. J. *J. Chem. Soc., Chem. Commun.* 1976, 990. Kimel, W.; Sax, N. W.; Kaiser, S.; Eichmann, G. G.; Chase, G. O.; Ofner, A. *J. Org. Chem.* 1958, 23, 153. (b) s-Collidine: Narwid, T. A.; Cooney, K. E.; Uskokovic, M. R. *Helv. Chim. Acta* 1974, 57, 771. (c) NaOAc: Camps, F.; Canela, R.; Coll, J.; Messeguer, A.; Roca, A. *Tetrahedron* 1978 34, 2179. (d) NaH: Tanabe, M.; Hayashi, K. *J. Org. Chem.* 1980, 102, 862.
(9) Ireland, R. E.; Mueller, R. *J. Am. Chem. Soc.* 1972, 94, 5897.
(10) Harris, T. M.; Murray, T. P.; Harris, C. M.; Gumulka, M. *J. Chem. Soc., Chem. Commun.* 1974, 362.
(11) All new compounds possessed spectral and analytical data in accord with their structures.
(12) Wilson, S. R.; Price, M. F. *J. Am. Chem. Soc.* 1982, 104, 1124.
(13) Steglich, W.; Hofle, G. *Angew. Chem., Int. Ed. Engl.* 1969, 981.