ether (50 mL) and trimethylphosphine (0.34 mL, 3.4 mmol). The solution was warmed to room temperature and stirred for 3 h. The solution was filtered, concentrated to ca. 30 mL, and cooled to −20 °C to afford off-white prisms of the product, yield 0.43 g (59%). IR (cm^{-1}): 2724 w, 2706 w, 1748 w, 1715 w, 1685 w, 1590 m, 1531 s, 1392 s, 1304 s, 1282 s, 1252 m, 1213 s, 1025 m, 1008 m, 946 s br, 876 w, 844 s, 728 s, 706 w, 667 w, 575 w, 535 s, 483 w. EPR (PhMe glass, −196 °C): 60, 172, 275, 355 mT.

Crystallographic Studies.[50] Single crystals of $Mn(Mes)Br_2(PMe_3)_2$ (**2b**), grown from diethyl ether, were sealed in thin-walled glass capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures followed by least-squares refinement with 25 reflections yielded the cell dimensions given in Table III.

Data were collected in one quadrant of reciprocal space ($\pm h,+k,+l$) by using measurement parameters listed in Table III. Systematic absences for $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) were consistent with the space group $P2_1/n$. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.324 and 0.276, respectively. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods, SHELX, weighted and unweighted difference Fourier syntheses, and full-matrix least-squares methods. The positions of the manganese, bromine, phosphorus, and five carbon atoms were deduced from an E map. Subsequent difference Fourier calculations revealed the positions of the remaining nonhydrogen atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 4.70/(\sigma(F_o)^2 + (pF_o)^2)$.

The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. Hydrogen atoms were included as fixed contributors in "idealized" positions with C–H = 0.95 Å. In the final cycle of least squares, anisotropic thermal coefficients were refined for the non-hydrogen atoms and a group isotropic thermal parameter was varied for the hydrogen atoms. Successful convergence was indicated by the maximum shift/error of 0.042 in the last cycle. Final refinement parameters are given in Table III. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors.

Acknowledgment. We thank the National Science Foundation (Grant CHE 89-17586) and the Office of Naval Research under their Young Investigator Award Program for support of this research and Lubrizol and Quantum Chemicals for fellowships to R.J.M. We particularly thank Dr. Scott Wilson and Charlotte Stern of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determination. G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990) and a Henry and Camille Dreyfus Teacher-Scholar Award (1988–1993).

Supplementary Material Available: Tables of final atomic coordinates, anisotropic thermal parameters, and calculated hydrogen atom positions for **2b** (3 pages); a listing of final observed and calculated structure factor amplitudes for **2b** (8 pages). Ordering information is given on any current masthead page.

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[50] For details of this data collection and refinement procedure, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977-4982.

Stereoselective Synthesis of Diacids by the Nickel Cyanide and Phase-Transfer-Catalyzed Carbonylation of Alkynols. Novel Dependency of Product Stereochemistry and Optimum Stirring Speed on the Nature of the Phase-Transfer Agent

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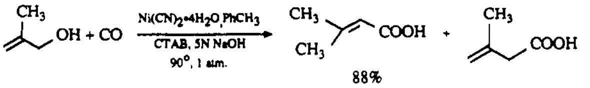
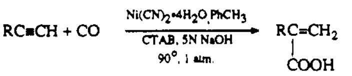
Alkynols react with carbon monoxide and catalytic amounts of nickel cyanide, under phase-transfer catalysis conditions [5 N NaOH, $PhCH_3$, $R_4N^+X^-$], to give unsaturated diacids in 83–95% yields. The stereoselectivity of the reaction is sensitive to the nature of the quaternary ammonium salt. Unusual stirring speed effects on the reaction rate were observed when tetrabutylammonium hydrogen sulfate or cetyltrimethylammonium bromide was used as the phase-transfer agent.

Carbonylation reactions are one of the most useful metal-catalyzed processes effected under phase-transfer conditions.[1] Recent investigations have indicated that nickel cyanide, a cheap metal catalyst, is effective for the carbonylation of a variety of organic substrates.[2-4] Of relevance to the present study are the observations that allyl alcohols can be directly carbonylated to acids (eq 1)[3] and that alkynes experience regiospecific hydrocarboxylation to unsaturated acids (eq 2).[4] It seemed



(1)



$$RC\equiv CH + CO \xrightarrow[\text{CTAB, 5N NaOH, 90°, 1 atm.}]{Ni(CN)_2\cdot 4H_2O,\ PhCH_3} \underset{\displaystyle COOH}{\underset{|}{RC}}{=}CH_2 \qquad (2)$$

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[1] Petrignani, J. F. *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; J. Wiley and Sons, Ltd.: New York, 1989; Vol. 5, pp 63-106.

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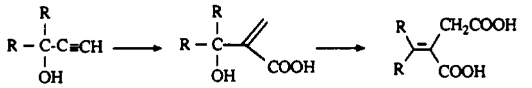
Table I. Phase-Transfer-Catalyzed Carbonylation of Alkynols[a]

alkynol	phase-transfer agent[b]	diacid, %[c]	product distribution E(4)	product distribution Z(5)
1, $n = 4$	TBAC	89		
1, $n = 5$	TBAC	86		
1, $n = 7$	TBAC	93		
3, R = CH_3	TBAC	83		
3, R = C_2H_5	TBAC	92	50	50
	CTAB	95	9	91
	β-CD	90	50	50
	PEG-400	90	50	50
	PEG-400/$CeCl_3$	92	32	68
3, R = $CH_2CH(CH_3)_2$	TBAC	90	44	56
	CTAB	95	7	93
	Aliquat 336	95	8	92
	$(C_4H_9)_4N^+HSO_4^-$	93	5	95
	$C_{12}H_{25}N(CH_3)_3^+Cl^-$	90	15	85
	$C_{14}H_{29}N(CH_3)_3^+Br^-$	92	5	95
	Briz 30	91	6	94
3, R = Ph	CTAB	88	89	11
	Briz 30	90	99.8	0.2

[a] Reaction conditions: alkynol (10 mmol), $Ni(CN)_2 \cdot 4H_2O$ (1.0 mmol), phase-transfer agent (0.2 mmol), 5 N NaOH (20 mL), $PhCH_3$ (45 mL), CO (1 atm), 95 °C, 8 h, 1200 rpm stirring speed. [b] TBAC = tetra-*n*-butylammonium chloride; CTAB = cetyltrimethylammonium bromide. [c] Isolated yields.

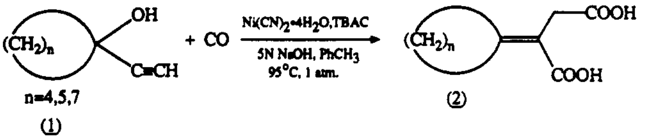
conceivable to us that alkynols could be converted to unsaturated diacids by hydrocarboxylation of the alkyne unit, followed by carbonylation of the in situ generated allylic alcohol (eq 3). Indeed, as illustrated below, the anticipated diacids are obtained in high yields from alkynols. Furthermore, the reaction occurs with high stereoselectivity by the use of appropriate phase-transfer agents.



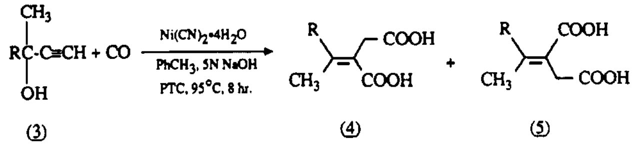
(3)

Results and Discussion

Treatment of 1-ethynylcyclopentanol (1, $n = 4$) with carbon monoxide and catalytic quantities of hydrated nickel cyanide, using toluene as the organic phase, 5 N sodium hydroxide as the aqueous phase, and tetra-*n*-butylammonium chloride (TBAC) as the phase-transfer agent, for 8 h at 95 °C and 1 atm, afforded the unsaturated diacid 2 in 89% isolated yield. The ratio of substrate/$Ni(CN)_2 \cdot 4H_2O$/TBAC was 10/1.0/0.2. Only 8% of 2 ($n = 4$) was obtained when the reaction was effected in the absence of the phase-transfer catalyst. Lower yields of diacid result at reduced base concentrations in the phase-transfer reaction (e.g. 3 N NaOH gives the diacid in 68% yield). Other ethynylcycloalkanols (1, $n = 5$, 7) experience nickel- and phase-transfer-catalyzed carbonylation in fine yields, as did 3-hydroxy-3-methyl-1-butyne (see Table I for results).



E-4 and *Z*-5 diacids can, in principle, be formed by using an alkynol, 3, where R is not a methyl group. Nickel-catalyzed carbonylation of 3 (R = C_2H_5) using TBAC as the phase-transfer catalyst, afforded a 1/1 mixture of 4 and 5 in 92% total yield of isolated products. The *Z*/*E* product ratios were determined by using NMR spectroscopy, by measurement of the *J* values for coupling of the protons of the olefinic methyl group of 4 or 5 with those of the methylene unit of CH_2COOH (i.e., homoallylic coupling), with the magnitude of the coupling constant being greater, for the E than for the Z isomer.[5] The same E/Z product distribution was found by using β-cyclodextrin[6] or PEG-400[7] as the phase-transfer catalyst. However, if cerium trichloride[2] is used in conjunction with the PEG-400 system then *Z*/*E* diacids are products in a ratio of 68/32. Much higher *Z*-selectivity [91/9 = *Z*/*E*] was realized by using cetyltrimethylammonium bromide (CTAB) as the phase-transfer agent. Different phase-transfer catalysts were used for the carbonylation of 3 (R = $CH_2CH(CH_3)_2$) in order to determine whether this interestiing dependence of the isomer distribution on the phase-transfer agent occurred with other alkynols. Analogous to 3 (R = C_2H_5), the alkynol 3 (R = $CH_2CH(CH_3)_2$) is carbonylated in good yield by using $Ni(CN)_2 \cdot 4H_2O$ and TBAC, but with low *Z*/*E* stereoselectivity. Likewise, CTAB gives good stereoselectivity for the *Z* diacid, in accord with the results attained for 3 (R = C_2H_5). Other quaternary ammonium salts, including tetrabutylammonium hydrogen sulfate, afford 5 (R = $CH_2CH(CH_3)_2$) as the predominant product. It is not clear why the stereoselectivity of the reaction is so different with the two tetra-*n*-butylammonium salts [Cl^-, HSO_4^-]. The surfactant Briz 30[8] is equally effective for the generation of *Z*-5 in good stereochemical control. Use of 3 (R = Ph) as the reactant, with either CTAB or Briz 30 as the phase-transfer agent, afforded the *E* diacid as the major isomer. The reversal in stereochemistry compared with the case where R = C_2H_5, $CH_2CH(CH_3)_2$ may be a consequence of the conjugation of the phenyl group with the α,β-unsaturated moiety when the phenyl and acid units are in a trans configuration.



The rate of nickel cyanide catalyzed carbonylation of 3,5-diethyl-1-hexyn-3-ol with time was followed at different stirring speeds. When TBAC was used as the phase-transfer agent, the rate of carbonylation increased with increasing stirring speed (Figure 1, 1200 > 900 > 600 rpm). However, use of either CTAB or tetra-*n*-butylammonium hydrogen sulfate as the phase-transfer catalyst resulted in a greater rate of carbonylation of 3 (R = $CH_2CH(CH_3)_2$) at 900 rpm than at 600, 1050, or 1200 rpm. This unusual behavior was also observed when 3 (R = C_2H_5) was employed as the reactant, with CTAB or TBAC as the quaternary ammonium salt. In addition, use of decalin as the organic phase for the carbonylation of 3 (R = $CH_2CH(CH_3)_2$) with CTAB as the phase-transfer agent gave the maximum rate at 900 rpm.

A possible mechanism for the reaction is illustrated in Scheme I (using 3). Hydrocarboxylation of the alkyne unit of 3 would give 6. Conversion of the latter to the nickelate 7 followed by attack by $Ni(CO)_3CN^-$, generated in situ from nickel cyanide,[2-4] can afford the allylnickel complex

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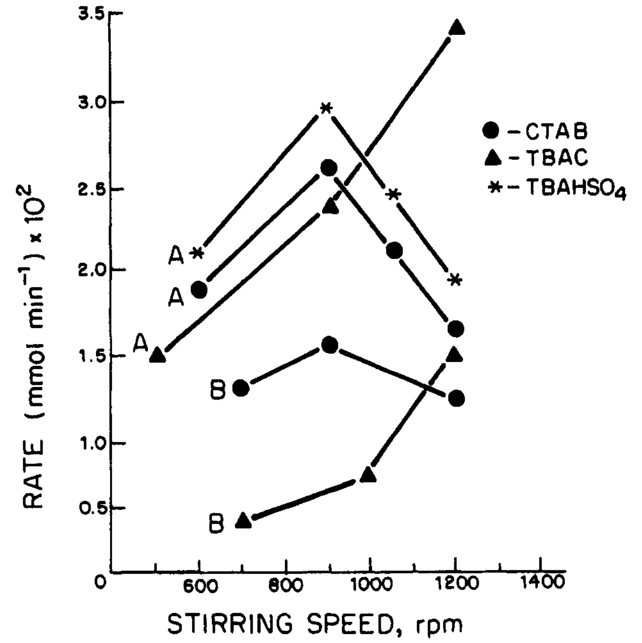
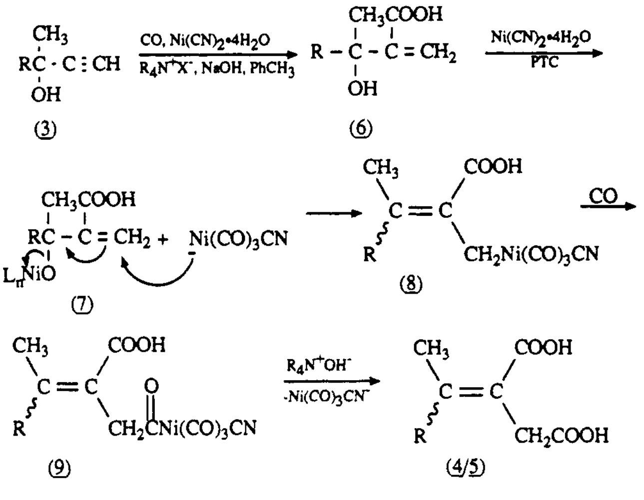


Figure 1. Dependence of the rate on the stirring speed for the carbonylation of (A) 3,5-diethyl-1-hexyn-3-ol and (B) 3-methyl-1-pentyn-3-ol.

Scheme I



8. The diacids (4/5) can then arise by carbonylation of 8 to 9, followed by base-induced carbon–nickel bond cleavage. The key step in determining the stereoselectivity of the process is the conversion of 7 to 8. As noted above, the low stereochemical control found when TBAC is used as the phase-transfer agent, compared with CTAB or $(C_4H_9)_4N^+HSO_4^-$, is mirrored by the diifferent rate–stirring speed profile exhibited when these phase-transfer catalysts are used. It is conceivable that the extent of ion pairing plays a major role in these processes. It is not likely that the degree of aggregation is important, since use of decalin and toluene as the organic phase gives the same rate–stirring speed dependence under otherwise identical conditions.

Let us compare the present methodology with that for reactions effected under homogeneous conditions. Modest yields of diesters, among other products, were obtained by palladium or cobalt complex catalyzed carbonylation of alkynols.[9] Similarly, Nogi and Tsuji[10] described the palladium chloride catalyzed carbonylation of alkynols in methanol to give mixtures of products, including the diester, in moderate yields. High pressures of carbon monoxide (100 atm) were required, and no assessment of the stereoselectivity of the reaction was made in either case.[9,10] In contrast, the nickel cyanide reaction proceeds cleanly and in high yields, with good stereochemical control of diacid formation realized by choice of the appropriate phase-transfer agent. The present study is the first demonstration, to our knowledge, of the dependence of stereochemistry of a phase-transfer reaction on the nature of the quaternary ammonium salt. Furthermore, these are the first cases where it has been found that the reaction rate shows such unusual dependence on the stirring speed, subject to the nature of the phase-transfer agent.

Experimental Section

General Data. A Fisher-Johns apparatus was used for melting point determinations. The following instrumentation was used to record spectra: Perkin-Elmer 783 (IR), Varian Gemini 200 and/or XL-300 (NMR), and VG7070E (MS). Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ. All of the alkynols used in this study were purchased from commercial suppliers and checked for purity (GC, NMR) prior to use. An IKAMAG-RET-G stirrer was used for this investigation. Reactions were carried out in a three-necked 100-mL flask containing a Teflon-coated magnetic stirring bar (2.54 cm × 0.95 cm o.d.).

General Procedure for the Phase-Transfer-Catalyzed Carbonylation of Alkynols with $Ni(CN)_2 \cdot 4H_2O$. A mixture of $Ni(CN)_2 \cdot 4H_2O$ (1.0 mmol), 5 N NaOH (20 mL), phase-transfer agent (0.2 mmol), and toluene (20 mL) was stirred under carbon monoxide for 2 h at 95 °C. The alkynol (10 mmol) in toluene (25 mL) was then added, in small portions, over a 1-h period. Stirring was continued, followed by gas chromatography, and when complete (8 h or less), the reaction mixture was separated with crushed ice added to the aqueous phase. The aqueous phase was neutralized with hydrochloric acid, and the diacid was isolated by ether extraction and drying ($MgSO_4$) of the ether extract, followed by rotary evaporation. Pure acid was obtained by crystallization from ether/hexane.

Several of the diacids are known materials: 2 (n = 5), mp 177–178 °C (lit.[10] mp 177–179 °C); 4/5 (R = CH_3), mp 165.0–165.4 °C (lit.[11] mp 162–163 °C). The following data were obtained for the other diacids.

2 (n = 4): IR (ν_{CO}) 1710, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (m, 4 H, CH_2), 2.10 (t, 2 H, CH_2), 2.50 (t, 2 H, CH_2), 3.00 (s, 2 H, CH_2COOH), 12.11 (s br, 2 H, COOH) ppm; ^{13}C NMR ($CDCl_3$) δ 25.0, 26.5, 33.3, 33.9 (ring methylene carbons), 35.9 (CH_2COOH), 118.1, 162.5 (olefinic carbons), 168.5, 172.7 (COOH) ppm; MS (m/e) 166, [M - H_2O]$^+$; mp 193.2–195.2 °C.

2 (n = 7): IR (ν_{CO} 1715, 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49 (m, 6 H, CH_2), 1.76 (m, 4 H, CH_2), 2.39 (t, 2 H, CH_2), 2.75 (t, 2 H, CH_2), 3.23 (s, 3 H, CH_2COOH), 12.15 (s br, 2 H, COOH) ppm; ^{13}C NMR ($CDCl_3$) δ 25.1, 25.6, 26.0, 26.3, 26.5, 32.3, 32.6 (ring methylene carbons), 35.2 (CH_2COOH), 121.6, 156.2 (olefinic carbons), 169.2, 172.9 (COOH) ppm; MS (m/e) 208, [M - H_2O]$^+$; mp 181.3–181.8 °C.

4/5 (R = C_2H_5): IR (ν_{CO}) 1710, 1670 cm^{-1}; ^{1}H NMR of 4 ($CDCl_3$) 1.04 (t, 3 H, CH_3), 2.12 (t, 3 H, CH_3), 2.21 (q, 2 H, CH_2CH_3), 3.39 (q, 2 H, CH_2COOH, J = 0.78 Hz), 12.0 (s, br, 2 H, COOH) ppm; ^{1}H NMR of 5 ($CDCl_3$) δ 1.06 (t, 3 H, CH_3), 1.87 (t, 3 H, CH_3), 2.54 (q, 2 H, CH_2CH_3), 3.37 (q, 2 H, CH_2COOH, J = 0.50 Hz), 12.11 (s br, 1 H, COOH) ppm; ^{13}C NMR of 4 ($CDCl_3$) δ 11.78 (CH_3CH_2), 20.0 (CH_3C=), 29.0 (CH_3CH_2), 34.9 (CH_2COOH), 121.7, 151.3 (olefinic carbons), 169.2, 172.5 (COOH) ppm; ^{13}C NMR of 5 ($CDCl_3$) δ 12.7 (CH_3CH_2), 20.2 (CH_3C=), 28.7 (CH_3CH); 35.3 (CH_2COOH), 121.5, 152.1 (olefinic carbons), 169.1, 172.7 (COOH) ppm; MS (m/e) 154, [M - H_2O]$^+$; mp 182.3–184.0 °C.

4/5 (R = $CH_2CH(CH_3)_2$): IR (ν_{CO}) 1708, 1670 cm^{-1}; ^{1}H NMR of 4 ($CDCl_3$) δ 0.91 (d, 6 H, $(CH_3)_2CH$), 1.88 (m, 1 H, $CH(CH_3)_2$),

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Organometallics **1991**, *10*, 807–812

2.10 (t, 3 H, CH_3), 2.12 (d, 2 H, $CH_2CH(CH_3)_2$), 3.42 (q, 2 H, CH_2COOH, J = 0.90 Hz), 12.08 (s br, 2 H, COOH) ppm; ^1H NMR of **5** ($CDCl_3$) δ 0.89 (d, 6 H, $(CH_3)_2CH$), 1.86 (t, 3 H, CH_3), 1.87 (m, 1 H, $CH(CH_3)_2$), 2.56 (d, 2 H, $CH_2CH(CH_3)_2$), 3.39 (q, 2 H, CH_2COOH, J = 0.56 Hz), 12.15 (s br, 2 H, COOH) ppm; ^{13}C NMR of **4** ($CDCl_3$) δ 21.1, 22.1 (methyl carbons), 26.7 ($CH_2CH(CH_3)_2$), 35.2 (CH_2COOH), 44.7 ($CH(CH_3)_2$), 123.0, 148.8 (olefinic carbons), 169.3, 172.9 (COOH) ppm; ^{13}C NMR of **5** ($CDCl_3$) δ 20.8, 22.3 (methyl carbons), 26.9 ($CH_2CH(CH_3)_2$), 35.5 (CH_2COOH), 43.6 ($CH(CH_3)_2$), 123.1, 149.4 (olefinic carbons), 169.4, 172.6 (COOH) ppm; MS (m/e) 182, $[M - H_2O]^+$; mp 169.5–169.8 °C.

4/**5** (R = Ph): IR (ν_{CO}) 1710, 1665 cm^{-1}; ^1H NMR of **4** ($CDCl_3$) δ 2.40 (t, 3 H, CH_3), 3.16 (q, 2 H, CH_2, J = 0.93 Hz), 7.31 (m, 5 H, Ph), 12.37 (s br, 2 H, COOH) ppm; ^1H NMR of **5** ($CDCl_3$) δ 2.13 (t, 3 H, CH_3), 3.53 (q, 2 H, CH_2, J = 0.60 Hz), 7.30 (m, 5 H, Ph), 12.33 (s br, 2 H, COOH); ^{13}C NMR ($CDCl_3$) δ 23.1 (CH_3), 36.9 (CH_2), 123.7, 126.8, 127.7, 128.7, 143.2, 149.5 (olefinic and aromatic carbons), 169.2, 172.8 (COOH) ppm; MS (m/e) 202, $[M - H_2O]^+$; mp 149.4–150.8 °C.

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research. We are indebted to Prof. G. W. Gokel for a valuable discussion and suggestions.

Opening of Oxirane Rings by the Conjugate Base of Pentacarbonyl(methoxymethylcarbene)chromium in the Presence of Boron Trifluoride Etherate: A General and Improved Synthesis of Pentacarbonyl(2-oxacyclopentylidene)chromium Compounds

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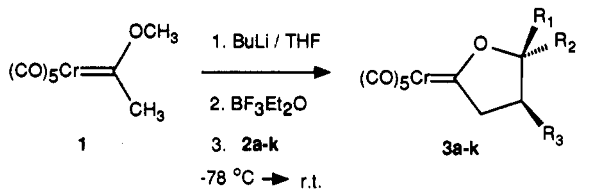
A modified procedure for the synthesis of new pentacarbonyl(2-oxacyclopentylidene)chromium compounds is reported. Its application to optically pure epoxides allowed us to obtain the corresponding optically pure cyclic chromium carbene complexes. The oxidation of the (2-oxacyclopentylidene)pentacarbonylchromium compounds led to the corresponding substituted γ-butyrolactones.

Introduction

Pentacarbonyl(alkoxyalkylcarbene)chromium complexes are well-known, useful substrates in organic synthesis.[1] Structural features unique to this type of compound, i.e., the presence of a pentacarbonylchromium residue and a carbon–chromium double bond, modulate the chemistry of these organometallics. The fact that the carbon–metal double bond can be easily cleaved under mild oxidative conditions and transformed into a carbonyl group gives additional versatility to these compounds. Thus, these complexes are already routinely employed as synthetic precursors of various derivatives of chemical and biological significance, such as β-lactams,[2] indole alkaloids,[3] cyclobutanones,[4] and anthracyclinone synthons.[5] For these reasons, the research in this area has been directed toward the synthesis of new complexed carbenes and their utilization as substrates for preparing useful derivatives.

In particular, one class of these derivatives, the pentacarbonyl(2-oxacyclopentylidene) chromium complexes, although very promising, has enjoyed little popularity in organic synthesis up to now. In 1974, Casey reported[6] the first synthesis of four pentacarbonyl(2-oxacyclopentylidene)chromium complexes obtained from the reaction of pentacarbonyl(methoxymethylcarbene)chromium and pentacarbonyl(ethylmethoxycarbene)chromium complexes with ethylene and propylene oxides. More recently, Doetz published[7] a new synthetic procedure for one of these compounds, the unsubstituted pentacarbonyl(2-oxacyclopentylidene)chromium, starting from $(CO)_5Cr{\cdot}OEt_2$ and 1-butyn-4-ol. Little data[8] are available on the chemical reactivity of these carbene derivatives, and their synthetic usefulness has yet to be fully exploited. Moreover, the synthetic procedure reported by Casey proved not to be

Scheme I



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