Phase Transfer Catalyzed Hydroxyacylation of Allenes

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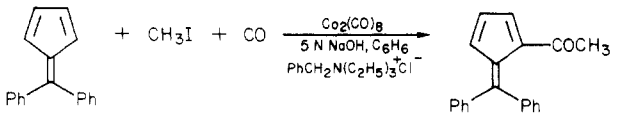
Phase transfer catalyzed reaction [NaOH, C_6H_6, $C_{16}H_{33}N(CH_3)_3^+Br^-$] of allenes with dicobalt octacarbonyl, methyl iodide, and carbon monoxide at room temperature and atmospheric pressure affords unsaturated hydroxy ketones and dienones. The latter are also produced without using phase-transfer conditions and in the absence (or presence) of methyl iodide. Mechanisms are proposed for the phase-transfer reaction.

Phase-transfer catalysis is an inexpensive, mild, and useful method for the generation of the cobalt tetracarbonyl anion or acetylcobalt tetracarbonyl from dicobalt octacarbonyl.[2] The produced species can effect the carbonylation of halides[3-5] and phase-transfer agents,[6] the formation of butenolides,[7] and the regiospecific acylation of dienes[8] and fulvenes (e.g., 1 → 2).[9]



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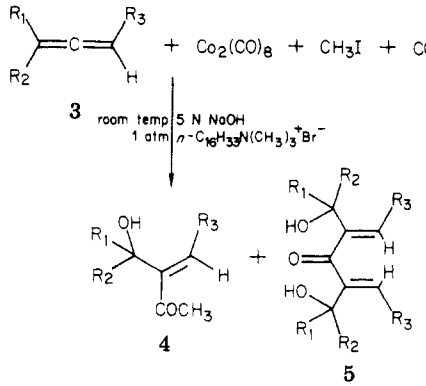
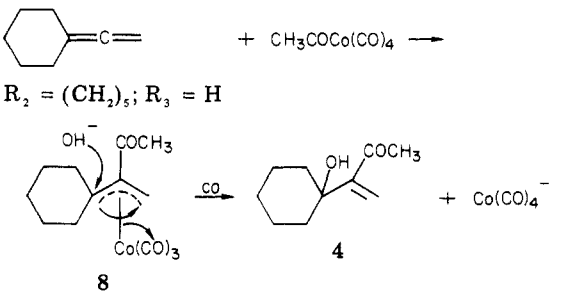
Allenes (1,2-dienes) can, in principle, undergo addition by the in situ generated acetylcobalt tetracarbonyl. We now report the interesting results of the phase transfer catalyzed reactions of allenes with dicobalt octacarbonyl.

Treatment of 1,2-undecadiene (**3**, $R_1 = C_8H_{17}$; $R_2 = R_3 = H$) with $Co_2(CO)_8$, methyl iodide, carbon monoxide, and cetyltrimethylammonium bromide as the phase-transfer catalyst in a two-phase system (5 N NaOH/C_6H_6) at room temperature afforded the unsaturated hydroxy ketone **4**



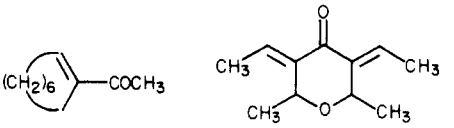
($R_1 = C_8H_{17}$; $R_2 = R_3 = H$) as the major product and the dienone **5** ($R_1 = C_8H_{17}$; $R_2 = R_3 = H$) as a byproduct. The hydroxyacylated product (**4**) was also formed by using 1,1-dimethylallene ($R_1 = R_2 = CH_3$; $R_3 = H$), *unsym*-pentamethyleneallene ($R_1 = R_2 = (CH_2)_5$; $R_3 = H$), and 1,2-cyclononadiene ($R_1 = R_3 = (CH_2)_6$; $R_2 = H$) as substrates, but not in the case of 1,3-dimethylallene (Table I).

Scheme I



Structural identification of **4** and **5** was based on analytical and spectral (IR, NMR, and mass spectra) data (Table I). All of the hydroxy ketones (**4**) and dienones (**5**) displayed OH stretching vibrations in the infrared region at 3350–3500 cm^{-1} and carbonyl and olefinic absorptions occurred at 1620–1665 cm^{-1}. The proton magnetic resonance spectra are also in accord with the assigned structures, and molecular ion peaks were observed in the mass spectra.

In addition to **4** and **5**, several other products were sometimes formed. The methyl ketone **6**, lacking a hydroxyl group, was a byproduct of the 1,2-cyclononadiene reaction and the interesting cyclic dienone **7** was isolated from the reaction where 1,3-dimethylallene was used as the substrate. The pyrone **7** may arise by cyclodehydration of **5** ($R_1 = R_3 = CH_3$; $R_2 = H$).



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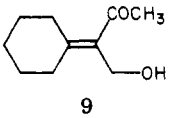
A possible pathway for the formation of the hydroxyacylated product **4** is given in Scheme I [illustrated for cyclohexylallene]. Addition of the in situ generated acetylcobalt tetracarbonyl to the allene would give the 2-acetyl-π-allylcobalt tricarbonyl complex **8**. Precedence for the occurrence of this type of reaction comes from the work by Otsuka and Nakamura[10] on the preparation of 2-acetyl-π-allylcobalt tricarbonyl from allene and acetylcobalt tetracarbonyl. Attack by hydroxide ion at the most substituted terminal carbon of the π-allyl unit would, on decomplexation, afford the hydroxy ketone **4**. It is noteworthy that none of the isomeric product **9** was obtained,



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the latter resulting from attack by hydroxide at the least

(1) E. W. R. Steacie Fellow, 1980–82.
(2) H. Alper, *Adv. Organomet. Chem.*, in press.
(3) H. Alper and H. des Abbayes, *J. Organomet. Chem.* **134**, C11 (1977).
(4) L. Cassar and M. Foa, *J. Organomet. Chem.* **134**, C15 (1977).
(5) H. des Abbayes and A. Buloup, *Tetrahedron Lett.*, **21**, 4343 (1980).
(6) S. Gambarotta and H. Alper, *J. Organomet. Chem.*, **194**, C19 (1980).
(7) H. Alper, J. K. Currie, and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, 311 (1978).
(8) H. Alper and J. K. Currie, *Tetrahedron Lett.* 2665 (1979).
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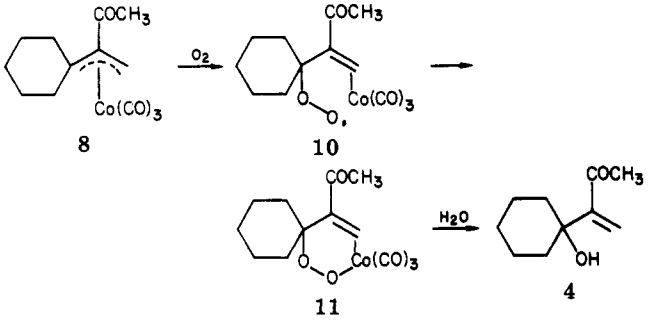
Table I. Products Obtained from the Phase Transfer Catalyzed Reactions of Allenes

allene 3	product[a]	% yield[b]	IR,[c] cm^{-1}	^1H NMR, δ[d]	mass spectrum, m/e
$R_1 = C_8H_{17}$; $R_2 = R_3 = H$	4	43	3440, 1660, 1620	0.85-1.35 (m, 17 H, C_8H_{17}), 2.35 (s, 3 H, $COCH_3$), 3.10 (br s, 1 H, OH), 4.43 (m, 1 H, CHOH), 5.96, 6.10 (m, 2 H, olefinic protons)	312
	5	19 (60)	3420, 1645, 1615	0.80-1.50 (m, 34 H, protons of octyl groups) 2.50 (br s, 2 H, OH), 4.48 (m, 2 H, CHOH), 5.93, 6.15 (each s, 4 H, olefinic protons)	366
$R_1 = R_2 = CH_3$; $R_3 = H$	4	23	3450, 1660, 1620	1.46 (s, 6 H, CH_3), 2.40 (s, 3 H, $COCH_3$), 3.50 (s, 1 H, OH), 6.02 (q, 2 H, olefinic protons)	128
	5	50 (75)	3425, 1645, 1630	1.45 (s, 12 H, CH_3), 3.90 (s, 2 H, OH), 5.65, 6.00 (each s, 4 H, olefinic protons)	180
$R_1 = R_2 = (CH_2)_5$; $R_3 = H$	4	40	3470, 1660, 1630	1.50-1.80 (m, 10 H, $(CH_2)_5$), 2.35 (s, 3 H, $COCH_3$), 3.90 (s, 1 H, OH), 5.55, 6.05 (each s, 2 H, olefinic protons)	168
	5	8 (70)	3450, 1650, 1630	1.50-1.80 (m, 20 H, $(CH_2)_5$), 3.60 (s, 2 H, OH), 5.65, 5.95 (each s, 4 H, olefinic protons)	278
$R_1 = R_3 = (CH_2)_6$; $R_2 = H$	4	38	3500, 1650 (br)	1.50-2.50 (m, 13 H, $(CH_2)_6$ and OH), 2.41 (s, 3 H, $COCH_3$), 4.20 (m, 1 H, CHOH), 6.91 (t, 1 H, CH=)	182
	6[e]	15	1640, 1620	1.30-2.40 (m, 14 H, $(CH_2)_7$), 2.35 (s, 3 H, $COCH_3$), 6.80 (t, 1 H, CH=)	166
$R_1 = R_3 = CH_3$; $R_2 = H$	5	9[f]	3350, 1665, 1635	1.37 (d, 6 H, $J = 7$ Hz, CH_3CHOH), 2.10 (d, 3 H, $J = 7$ Hz, CH_3CH=), 2.13 (d, 3 H, CH_3CH=), 3.90 (br s, 2 H, OH), 4.50 (m, 2 H, CHOH), 6.10 (q, 1 H, $CHCH_3$), 6.14 (q, 1 H, $CHCH_3$)	198
	7	14	1675, 1618	0.95, 1.16 (d, 6 H, $J = 7$ Hz, methyls on saturated carbons), 1.92, 1.97 (d, 6 H, methyls on unsaturated carbons), 4.15 (m, 2 H, $CHCH_3$), 5.62, 5.66 (each q, 2 H, $CHCH_3$)	180

[a] Satisfactory (±0.4%) C, H analyses were obtained for all products. [b] Yields are of analytically pure products. Yields in parentheses refer to reactions effected under non-PTC conditions. [c] $CHCl_3$ solution. [d] $CDCl_3$ with Me_4Si as internal standard. [e] Compound 12 was obtained in 40% yield under non-PTC conditions: IR ($CHCl_3$) 1685, 1650 cm^{-1}; NMR ($CDCl_3$) δ 0.9-3.1 (m, 26 H, saturated protons), 6.70 (t, 2 H, olefinic protons); mass spectrum, m/e 272 (M^+). [f] A mixture of cis and trans isomers was formed.

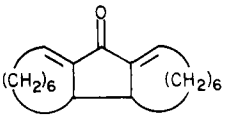
Scheme II



substituted terminal carbon of the π-allyl complex (8). This regiospecificity of the hydroxyacylation reaction is general and, in our opinion, surprising since one would expect nucleophilic attack at 8 (and related complexes) to occur at the least hindered center.

Since 4 (and 5) is formed on exposure of the reaction mixture to air, an alternative radical pathway involving oxygen merits consideration (Scheme II). Attack by oxygen at the most substituted carbon of 8 would give the diradical 10 which could then couple intramolecularly to form 11. Cleavage of the peroxy linkage by moisture would then afford the observed product 4.

The dienone 5 does not contain an acetyl group, suggesting that this product may be formed without resorting to phase-transfer techniques. Indeed, treatment of 3 ($R_1 = R_2 = (CH_2)_5$, $R_3 = H$; $R_1 = R_2 = CH_3$, $R_3 = H$; $R_1 = C_8H_{17}$, $R_2 = R_3 = H$) with cobalt carbonyl in anhydrous benzene (carbon monoxide atmosphere), in the presence or absence of methyl iodide, afforded 5 as the only product in 60–75% yields (Table I). An exception occurred with 1,2-cyclononadiene (3, $R_1 = R_3 = (CH_2)_6$; $R_2 = H$) which gave the cyclic dienone 12 in 40% yield.



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In conclusion, although the yields are not high, the phase transfer catalyzed hydroxyacylation of allenes constitutes a simple, "one-pot" procedure for the synthesis of an interesting class of compounds which are, to our knowledge, not easily accessible by other means. An investigation of the chemistry of the unsaturated hydroxy ketones (e.g., cyclization reactions) is in progress.

Experimental Section

General Procedures. Elemental analyses were carried out by Canadian Microanalytical Service, Ltd, Vancouver, Canada. Infrared spectra were recorded by using a Unicam SP1100 spectrometer, equipped with a calibration standard. A Varian MS9 was used for mass spectral determinations, and a T60 for NMR spectra.

Cobalt carbonyl was purchased from Pressure Chemical Co. and was used as received. 1,1-Dimethylallene and 1,3-dimethylallene were commercial products (Albany International Corp). 1,2-Undecadiene,[11] cyclononallene,[12] and *unsym*-pentamethyleneallene[13] were synthesized according to literature procedures.

General Procedure for Phase Transfer Catalyzed Hydroxyacylation of Allenes. A mixture of benzene (20 mL), 5

(11) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).
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N NaOH (20 mL), cetyltrimethylammonium bromide (0.10 g), and $Co_2(CO)_8$ (10 mmol) was stirred for 3 h at room temperature in a CO atmosphere. Methyl iodide (5 mL) was added to the stirred solution, followed by the allene (10 mmol), and the reaction mixture was stirred for an additional 2–3 h. The reaction mixture was then stirred in air until the decomposition of the organometallic species was complete. The phases were separated (the aqueous phase did not contain any organic products), and the organic phase was washed with water, dried, and concentrated. Separation of the reaction products was achieved by chromatography on silica gel, using hexane–ether as eluant (4 was eluted before 5 in all cases). Phenylallene is cleaved under PTC conditions.[14]

General Procedure for Reaction of Allenes with $Co_2(CO)_8$ in Benzene. To $Co_2(CO)_8$ (10 mmol) in benzene (20 mL) was added the allene (10 mmol). The solution was stirred under CO for 1 day and then exposed to air. Workup was effected as described for the organic phase in the phase transfer catalyzed process.

(14) H. Alper and J. K. Currie, unpublished results.

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Registry No. 3 ($R_1 = C_8H_{17}$; $R_2 = R_3 = H$), 56956-46-8; **3** ($R_1 = R_2 = CH_3$; $R_3 = H$), 598-25-4; **3** ($R_1 = R_2 = (CH_2)_5$; $R_3 = H$), 5664-20-0; **3** ($R_1 = R_3 = (CH_2)_5$; $R_2 = H$), 7124-40-5; **3** ($R_1 = R_3 = CH_3$; $R_2 = H$), 591-96-8; **3** ($R_1 = R_3 = (CH_2)_6$; $R_2 = H$), 1123-11-1; **4** ($R_1 = C_8H_{17}$; $R_2 = R_3 = H$), 76584-04-8; **4** ($R_1 = R_2 = CH_3$; $R_3 = H$), 76584-05-9; **4** ($R_1 = R_2 = (CH_2)_5$; $R_3 = H$), 76584-06-0; **4** ($R_1 = R_3 = (CH_2)_5$; $R_2 = H$), 76599-29-6; **5** ($R_1 = C_8H_{17}$; $R_2 = R_3 = H$), 76584-07-1; **5** ($R_1 = R_2 = CH_3$; $R_3 = H$), 76584-08-2; **5** ($R_1 = R_2 = (CH_2)_5$; $R_3 = H$), 76584-09-3; (*E,E*)-**5** ($R_1 = R_3 = CH_3$; $R_2 = H$), 76584-10-6; (*Z,Z*)-**5** ($R_1 = R_3 = CH_3$; $R_2 = H$), 76584-11-7; (*E,Z*)-**5** ($R_1 = R_3 = CH_3$; $R_2 = H$), 76584-14-0; **6**, 17339-74-1; **7**, 76584-12-8; **12**, 76584-13-9; $Co_2(CO)_8$, 10210-68-1; CH_3I, 74-88-4; CO, 630-08-0.

Alkylation of Allylic Derivatives. On the Regio- and Stereochemistry of Alkylation of Allylic Alcohols by the Murahashi Method

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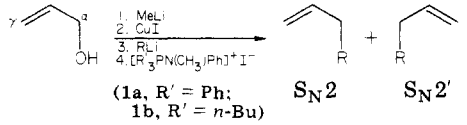
Direct alkylation of allylic alcohols by the Murahashi method has been reinvestigated. This four-step, one-pot process evidently involves formation of the lithium (allyloxy)alkylcuprate (**2**) followed by reaction with (methylphenylamino)triphenylphosphonium iodide (**1a**) or the corresponding tributylphosphonium iodide (**1b**). Contrary to earlier implications, the regiospecific and stereospecific anti γ-alkylation is independent of which aminophosphonium reagent is used. Presumably the final step involves alkylation of the (allyloxy)phosphonium ion (**3**) by $LiCu(R)(N(CH_3)Ph)$. This mixed cuprate also alkylates allylic carboxylates with about the same regio- and stereochemistry as for the Murahashi direct alkylation of the corresponding allylic alcohol. A general mechanism is presented that suggests that the regiochemistry of alkylation of allylic derivatives depends on the nature of the ancillary ligand in the alkylating cuprate.

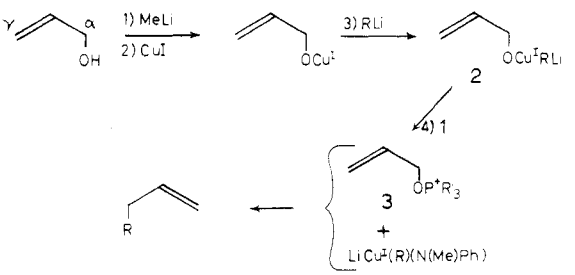
In connection with our investigation of the regio- and stereochemistry of alkylation of allylic carboxylates with dialkyl and mixed cuprates, we were interested in the direct alkylation of allylic alcohols reported by Murahashi and co-workers.[2] This four-step, one-pot process is shown by eq 1.



(**1a**, R' = Ph; **1b**, R' = *n*-Bu) S_N2 S_N2' (1)

In the initial report,[2a] (methylphenylamino)triphenylphosphonium iodide (**1a**) was used in step 4, and there was no indication of regiospecificity—a number of primary allylic alcohols were investigated, and all gave primarily the unrearranged α-alkylation product. More recently,[2b] the tributylphosphonium iodide **1b** was used instead of **1a**, and S_N2' regiospecificity (γ-alkylation) was observed. For example, cinnamyl alcohol and the isomeric α-phenylallyl alcohol undergo 96% and 100% γ-alkylation.[2b] Similarly, 5-methyl-2-cyclohexenol (**4**) undergoes 93% γ-alkylation. In the latter case it was shown that alkylation is also stereospecific and gives the anti alkylation product.

Scheme I. Steps Involved in the Direct Alkylation of Allylic Alcohols



We now report that the difference in regiochemistry in these reports[2] does not result from using different aminophosphonium reagents (**1a** and **1b**) but instead is due to another change in the experimental procedure. In fact, under the same conditions, the regiospecificity and stereospecificity are the same with **1a** and **1b** as would be expected from the mechanistic pathway proposed by Murahashi.[2b]

(1) National Science Foundation Fellow, 1977–1980.
(2) (a) Tanigawa, Y.; Kanamaru, H.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1977**, *99*, 2361. (b) Tanigawa, Y.; Ohta, H.; Sonoda, A.; Murahashi, S.-I. *Ibid.* **1978**, *100*, 4610.

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