ft × 0.01 in. SF-96) revealed the presence of unreacted **3**, octalone **5**, and a second product. The results from various runs are summarized in Table I. From one run, compound **5** was isolated by preparative vpc (10 ft × 0.25 in. Carbowax 20M) and identified by infrared and nmr spectra.[5]

Registry No.—Cyclobutane, 287-23-0; **3,** 17159-66-9.

Acknowledgments.—This investigation was supported by Public Health Service Research Grant No. AI-07765-01 from the National Institute of Allergy and Infectious Diseases.

Reaction of Dichlorocarbene with Enol Ethers. IX. Ethoxycycloheptadiene[1]

WILLIAM E. PARHAM, FRED M. PARHAM, JOSEPH F. DOOLEY, AND MARCUS K. MEILAHN

School of Chemistry of the University of Minnesota, Minneapolis, Minnesota 55455

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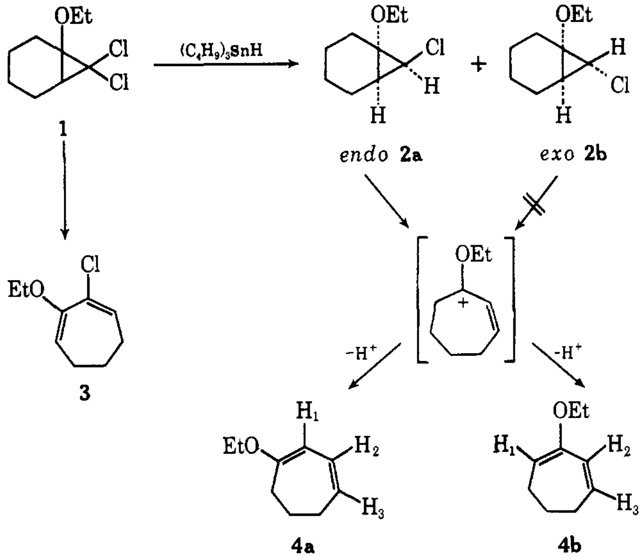
Ring expansion of monohalocyclopropanes derived from cyclic enol ethers appeared, by analogy with the chemical behavior of the corresponding dihalo derivatives,[2] to be an attractive synthetic route to cyclic diene ethers and cyclic unsaturated ketones. This paper describes the synthesis of 1-ethoxy-1,3-cycloheptadiene (**4a**) and certain derivatives of this system.

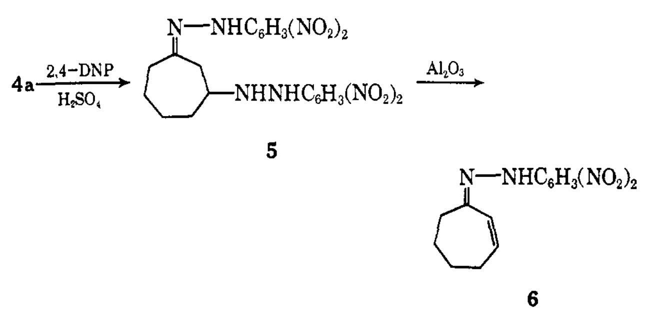
Reduction of 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (**1**) with tri-*n*-butyltin hydride[3] gave a mixture of *endo*- and *exo*-1-ethoxy-7-chloro[4.1.0]heptane which was separated in 35 and 6% yield, respectively, by fractional distillation. The configurations of the isomeric chlorocyclopropanes were assigned on the basis of their nmr spectra. Compound **2a** showed a doublet for the cyclopropyl hydrogen centered at 3.13 ppm with $J = 9.0$ Hz; **2b** exhibited a doublet at 2.59 ppm with $J = 4.4$ Hz. In cyclopropane systems *cis* coupling constants are known to be larger than *trans* coupling constants,[4] and the values observed are in close agreement with those reported[3] for *endo*- and *exo*-chloronorcaranes (*endo*, triplet, 3.14 ppm, $J = 7.5$ Hz; *exo*, triplet, 2.56 ppm, $J = 3.7$ Hz).

Ring expansion of halocyclopropanes are thought to occur by ionization of the carbon–chlorine bond,[5,6] with concerted ring opening, in which the substituents *trans* to the leaving group rotate outward.[7,8] Application of the Woodward–Hoffman selection rules[7] to 2 suggested that **2a** should undergo ring expansion much more readily[9] than **2b**, and this order of reactivity was confirmed experimentally.



Reaction of **2a** with refluxing pyridine gave ethoxycycloheptadiene (**4**) in 56% yield, while **2b**, under identical conditions, gave only recovered starting material. Ring expansion of **2a** might be expected to give either of two dienes (**4a** and/or **4b**). The nmr spectrum of the product **4** showed a single sharp quartet for the ethoxy methylene protons and vpc analysis showed a single peak. The absorption in the vinyl proton region was complex and consisted of two multiplets centered at 4.72 ppm (wt 1) and 5.40 ppm (wt 2). The most shielded vinyl proton in **4a** and **4b** must be H_1 owing to the conjugation with the ethoxy group. Decoupling of the vinyl proton at 4.72 ppm from the allylic protons simplified the pattern to a sharp doublet ($J = 8.5$ Hz) which is only compatible with **4a**, and the assignment of the structure is made on this basis. It is of interest to note that the only product reported by treatment of **1**, under identical conditions, was 2-ethoxy-3-chloro-1,3-cycloheptadiene (**3**) which was isolated in 83% yield.[2b]

Reaction of **4a** with 2,4-dinitrophenylhydrazine reagent[10] gave a diadduct (mp 170–171°) with composition in agreement with that calculated for **5**.[11] Chromatography of the product **5** on alumina gave in high



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[1] This work was supported by Grants GP-3357 and GP-6169X from the National Science Foundation.

[2] (a) W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Amer. Chem. Soc.*, **84**, 1755 (1962); (b) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *ibid.*, **87**, 321 (1965); (c) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 926 (1967).

[3] D. Seyferth, H. Yamozaki, and D. L. Alleston, *ibid.*, **28**, 703 (1963).

[4] (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) V. Schöllkopf and G. J. Lehmann, *Tetrahedron Lett.*, 165 (1962); (c) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Amer. Chem. Soc.*, **84**, 4985 (1962).

[5] (a) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *ibid.*, **78**, 1437 (1956); (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 924 (1967).

[6] W. E. Parham and E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

[7] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

[8] (a) C. H. DePuy, L. G. Swack, J. W. Hauser, and W. Wiedimann, *ibid.*, **87**, 4006 (1965); (b) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

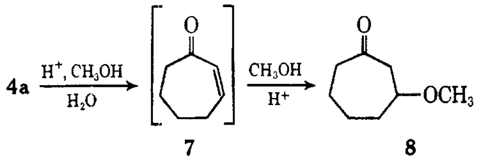
[9] Models show an energetically unfavorable bending strain imposed on the carbon skeleton in the transition state for such a reaction of **2b**.

[10] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 219.

[11] A diadduct presumably formed from 2-cycloheptenone has been reported to melt at 170 and 164°. *Cf.* (a) R. Jacquier and R. Fraisse, *Bull. Soc. Chim. Fr.*, 108 (1957); (b) J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, **28**, 3356 (1963).

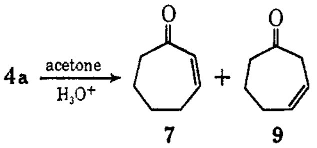
yield the 2,4-dinitrophenylhydrazone **6** as a red crystalline solid.

Hydrolysis of **4a** in acidic methanol–water gave a mixture composed principally of the previously unreported ether **8** (53% yield). This ether was the product expected by the addition of methanol to the intermediate **7**, and its structure was readily deduced from composition and spectral data (see the Experimental Section). The ether **8** reacted with 2,4-dinitrophenylhydrazine reagent[10] to give the diadduct **5**, identical with that obtained from **4a**.[12]



7 8

Hydrolysis of **4a** in acidic aqueous acetone, with subsequent distillation of the product, gave a 40% yield of a mixture of two $C_7H_{14}O$ ketones. The infrared spectrum of the product (C=O at 1704 and 1660 cm^{-1}) suggested it to be a mixture of **7** and **9**[13] and the ultraviolet spectrum of the mixture suggested that the composition was 62% of **7** and 38% of **9**; the nmr spectrum of the mixture was compatible with this assignment (see the Experimental Section). The formation of such a mixture of ketones from **4** was not indicative of the structure of the diene (**4a** or **4b**), since both **7** and **9** are readily equilibrated in acid solution to a similar mixture.[14]



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Experimental Section

Conversion of 1-Ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (1) into *endo*- and *exo*-1-Ethoxy-7-chlorobicyclo[4.1.0]heptane (2).—Tri-*n*-butyltin hydride (31.8 g, 0.11 mol) was added dropwise to 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane[2a] (23.1 g, 0.11 mol) which was vigorously stirred and maintained at 65° under an atmosphere of dry nitrogen. After the addition was completed, the temperature of the mixture was raised to 75–78° for 90 min. The mixture of *endo* and *exo* **2** (14.4 g, 75%) was then distilled from the reaction mixture [bp 48–59° (0.6 mm)]. Redistillation of this product through a spiral wire column gave 6.74 g (35%) of *endo*-1-ethoxy-7-chlorobicyclo[4.1.0]heptane (**2a**) [bp 41–44° (0.9 mm); $n^{24.5}$D 1.4730)] and 1.08 g (6%) of *exo*-1-ethoxy-7-chlorobicyclo[4.1.0]heptane (**2b**) [bp 52–54° (0.9 mm); $n^{24.5}$D 1.4762].

The infrared spectrum of **2a** showed absorptions at 2920, 2850, 1438, 1375 cm^{-1} (CH_2), 1164, 1107 (OC_2H_5), and 700 (CCl); nmr (CCl_4), δ 1.0–2.4 (m, 12), 3.13 (d, 1, *J* = 9.0 Hz, HCCl), and 3.40 ppm (q, 2, *J* = 7.0 Hz, OCH_2CH_3).

The infrared spectrum of **2b** showed absorptions at 2920, 2850, 1447, 1386 cm^{-1} (CH_2), 1194, 1174, 1118 (OC_2H_5), and 750 (CCl); nmr (CCl_4), δ 0.95–2.26 (m, 12), 2.59 (d, 1, *J* = 4.4 Hz, HCCl), and 3.40 ppm (q, 2, *J* = 7.0 Hz, OCH_2CH_3).

Anal. Calcd for $C_9H_{15}OCl$: C, 61.92; H, 8.57; Cl, 20.54. Found for **2a**: C, 62.04; H, 8.72; Cl, 20.61. Found for **2b**: C, 61.53; H, 8.46; Cl, 20.74.

1-Ethoxy-1,3-cycloheptadiene (4a).—A solution of **2a** (7.18 g, 0.041 mol) in pyridine (15 ml) was heated at reflux for 75 min under an atmosphere of dry nitrogen. Ether was added to the cooled solution, the mixture was filtered, and the filtrate was concentrated on a rotary evaporator. The residue was distilled to give 3.40 g (56%) of 1-ethoxy-1,3-cycloheptadiene (**4a**): bp 44–46° (1.2 mm); n^{25}D 1.500; ir 2900, 1435, 1380 (CH_2), 1637, 1613 (C=C), and 1235, 1171, 1145 cm^{-1} (OC_2H_5); uv max (95% EtOH), 261 mμ (ε 8960); nmr (CCl_4), δ 1.23 ppm (t, 3, *J* = 7.0 Hz, OCH_2CH_3), 3.55 (q, 2, *J* = 7.0 Hz, OCH_2CH_3), 1.50–2.05 (m, 2, CH_2), 2.05–2.55 (m, 4, CH_2—C=C), 4.72 (m, 1, CH=COC_2H_5), and 5.40 (m, 2, CH=C).

Anal. Calcd for $C_9H_{14}O$: C, 78.34; H, 10.12. Found: C, 78.15; H, 10.14.

Attempted Ring Expansion of *exo*-1-Ethoxy-7-chlorobicyclo[4.1.0]heptane (2b).—A solution of **2b** (0.89 g, 0.051 mol) in pyridine (5 ml) was heated at reflux for 1 hr. The mixture was cooled and ether (*ca.* 10 ml) was added. The ether solution was decanted from some black tarry precipitate. The tarry material was washed further with ether and the combined ether extracts were concentrated on a rotary evaporator. The product was chromatographed on alumina using petroleum ether (bp 60–68°) as the eluent, but only recovered **2b** (0.63 g, 71%) was obtained.

3-Methoxycycloheptanone (8).—A solution of **4a** (1.74 g, 0.010 mol) in methanol (10 ml), water (1 ml), and 12 *N* HCl (0.5 ml) was heated at reflux for 45 min. The mixture was cooled, poured into water (100 ml), and extracted with ether. The combined ether extracts were dried (Na_2SO_4) and concentrated on a rotary evaporator. The residue was distilled to give 0.76 g (53%) of 3-methoxycycloheptanone (**8**): bp 61–63° (1.6 mm); n^{25}D 1.4660; ir 2915, 2840, 1450, 1334 (CH_2), 1692 (C=O), and 1085 cm^{-1} (OCH_3); uv max (95% EtOH), 228 mμ (ε 418); nmr (CCl_4), δ 3.46 ppm (m, 1, $CHOCH_3$), 3.28 (s, 3, OCH_3), 2.65 [m, 2, CO-$CH_2CH(OCH_3)$], 2.33 (m, 2, CH_2CO), and 1.53–1.96 (m, 6, CH_2).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.63; H, 9.85. Found: C, 67.60; H, 9.40.

Hydrolysis of 4a to 2- and 3-Cycloheptenone.—A solution prepared from **4a** (2.8 g, 0.021 mol), acetone (8 ml), water (2 ml), and 12 *N* HCl (0.5 ml) was heated at the reflux temperature for 1 hr. The solution was cooled and poured into water (100 ml). The mixture was extracted with ether, and the combined ether extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator. The residue was distilled to give 0.88 g (40%) of a mixture of 2- and 3-cycloheptenone, **7** and **9**, respectively: bp 49–51° (3.7 mm); n^{25}D 1.4892 [lit.[12a] for a similar mixture: bp 31° (0.5 mm); n^{21}D 1.4913]; ir 1704 cm^{-1} (C=O), 1660 (C=C—C=O);[13] uv max (95% EtOH), 228 mμ (ε 6200) and 284 (23) [lit.[13] for 2-cycloheptenone (95% EtOH) 228 mμ (ε 10,060), for 3-cycloheptenone[15] (95% EtOH) 284 mμ (ε 80)]. On the basis of the extinction coefficient of 2-cycloheptenone the composition of the isomeric mixture was estimated to be 62% 2-cycloheptenone and 38% 3-cycloheptenone. The nmr spectrum (CCl_4) of the isomeric mixture showed peaks at δ 6.57 and 6.38 ppm (t of d, 0.56, $CH_{2X}CH_B=CH_ACO$, $J_{BX} \cong 5.5$ Hz and $J_{AB} \cong 11.8$ Hz) (lit.[14] J_{BX} = 5.5 Hz, J_{AB} = 12.1 Hz), 5.40–5.98 (m, 1.44, COCH=C and CH=C), 3.13 (m, 0.88, $COCH_2C$=C), 2.18 (m, 4, $COCH_2$ and CH_2C=C), and 1.62 (m, 3.12, CH_2). The composition of the mixture was estimated to be 56% of **7** and 44% of **9** on this basis.

Anal. Calcd for $C_7H_{10}O$: C, 76.47; H, 9.08. Found: C, 76.35; H, 9.35.

Preparation of 5 and 6.—When a sample of diene **4a**, the methoxy ketone **6**, or the mixture of ketones, **7** and **9**, in ethanol were added to excess 2,4-dinitrophenylhydrazine reagent,[10] an orange-brown precipitate formed immediately. The mixture was allowed to stand overnight and the precipitate was recrystallized from ethyl acetate to give good yields of a red-brown solid (**5**): mp 170–171°;[11] uv max (95% EtOH), 362 mμ (ε 15,500) and 269 (17,200) [lit.[11b] uv max (ethyl acetate) 352 mμ (ε 91,000), shoulder 422 (4500)].

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[12] The isomeric 2- and 4-methoxycycloheptanones are reported to give monoadducts with 2,4-dinitrophenylhydrazine. *Cf.* (a) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 607 (1954); (b) D. W. Adamson and J. Kenner, *ibid.*, 181 (1939).

[13] J. Maclean and R. P. A. Sneeded [*Tetrahedron*, **21**, 31 (1965)] report C=CC=O at 1670–1655 cm^{-1} for **7** and C=O at 1704 cm^{-1} for **9**.

[14] Equilibration of **7** or **9** in refluxing benzene with a *p*-toluenesulfonic acid catalyst affords a crude mixture composed of 73% of **7** and 27% of **9** as determined by vpc. The distilled mixture of ketones was composed of 64% of **7** and 38% of **9** as determined by ultraviolet spectroscopy: *cf.* N. Heap and G. H. Whitham, *J. Chem. Soc., B*, 164 (1966).

[15] A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4846 (1962).

Anal. Calcd for $C_{19}H_{20}N_8O_8$: C, 46.73; H, 4.13; N, 22.95. Found: C, 46.78; H, 4.11; N, 23.11.

Chromatography of this material on alumina using petroleum ether–benzene (60:40) gave **6** in good yields as a red solid: mp 140–141° (lit.[12a,16] 122°, 141°); uv max (95% EtOH), 372 mμ (ε 25,500) [lit.[12a] uv max ($CHCl_3$), 372 mμ (ε 21,000)].

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.51; H, 4.96; N, 19.59.

Registry No.—Dichlorocarbene, 75-09-2; **2a,** 17159-67-0; **2b,** 17159-68-1; **4a,** 17159-69-2; **7,** 1121-66-0; **8,** 17159-70-5; **9,** 1121-64-8.

[16] W. Triebs and P. Grossman, *Ber.*, **92**, 267 (1959).

On the Reaction of (+)-Tris[(*S*)-1-methylpropoxy]methane with Carbon Monoxide and Hydrogen

F. Piacenti, M. Bianchi, and P. Pino

Institute of Industrial Organic Chemistry, University of Pisa,
and Centro Nazionale di Chimica dei Composti di Coordinazione
ed Elemento Organici (C. N. R.); Laboratorio di Pisa,
Pisa, Italy

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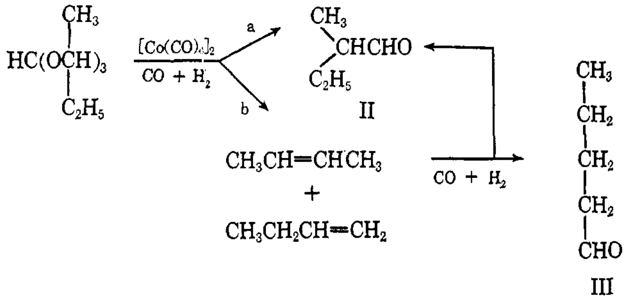
The synthesis of aldehydes from orthoformic esters, CO and H_2 has been already investigated to determine its possibilities and limitations as a synthetic method[1,2] and a mechanism has been suggested to rationalize its course.[3]

In order to get a better understanding of the reaction mechanism and stereochemistry, (+)-tris[(*S*)-1-methylpropoxy]methane (I) (optical purity 18.2%) was treated with CO and H_2 (Chart I) in the presence of $[Co(CO)_4]_2$.



n-Pentanal (III) and 2-methylbutanal (II) were obtained (Table I); the ratio between II and III was determined by vpc on the crude products and was found to be different in the two experiments (expt 1 and 2, Table I) carried out under different CO pressures. The optical purity of II was determined as previously described[4,5] and was lower at lower CO pressures.

As previously shown,[2] II is formed both directly from the ortho ester (path a) and by hydroformylation of the butenes formed by the decomposition of I probably *via* alkylcobalt carbonyls[3] (path b). The amount of II coming from path b, which must be racemic, can be roughly calculated from the amount of III formed and the known isomeric distribution of the hydroformylation products of butenes.[6] From the above data and considering that, as shown by preliminary experiments carried out on II, the maximum racemization of II under reaction conditions is 12 [illegible] 4%, it appears (Table II) that in both experiments the formation of II directly from I (path a) occurs with complete inversion and little racemization.

These results are inconsistent with an S_N1 nucleophilic substitution to the saturated carbon atom, as such a mechanism would lead to extensive racemization, and an S_N2 nucleophilic substitution to the saturated carbon atom is strongly suggested.

To gain evidence on the nature of the nucleophile, $HCo(CO)_4$ was treated with a large excess of racemic I at 0° under N_2 at atmospheric pressure. In fact, $HCo(CO)_4$ dissociates in polar solvent giving rise to the formation of the $[Co(CO)_4]^-$ anion.[7]

After addition of $P(C_6H_5)_3$, *sec*-$C_4H_9COCo(CO)_3P(C_6H_5)_3$ could be isolated and identified by comparing its ir spectrum with that of an authentic sample.[8]

In another experiment, racemic I was treated with CO and H_2 in the presence of $NaCo(CO)_4$. No reaction occurred at 0° and very limited gas absorption was noticed at 100° in several hours, accompanied by extensive decomposition of the orthoformic ester and a very limited formation of aldehydes.

Considering then that $[Co(CO)_4]_2$ under reaction conditions is mainly transformed into $HCo(CO)_4$[9] an attractive mechanism for the formation of II through path a involves a nucleophilic attack by the $[Co(CO)_4]^-$ anion on the protonated ortho ester (Chart II).

Similar nucleophilic attacks by $[Co(CO)_4]^-$ have been suggested in other carbonylations[10] and particularly in the carbonylation of sugar halides occurring with inversion of configuration.[11]

However, taking into account that in some carbonylations $HCo(CO)_4$ does not behave like a proton donor, even in oxygenated solvents, and that other cobalt carbonyl anions of higher complexity might be the true catalytic species in carbonylations,[12] the above scheme (Chart II) should be considered more an attempt to rationalize the experimental results than a proper representation of the reaction mechanism.

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[1] F. Piacenti, C. Cioni, and P. Pino, *Chem. Ind.* (London), 1240 (1961).

[2] F. Piacenti, *Gazz. Chim. Ital.*, **92**, 225 (1962).

[3] P. Pino, F. Piacenti, and P. P. Neggiani, *Chim. Ind.* (Milan), **44**, 1367 (1962).

[4] L. Lardicci and R. Rossi, *Atti Soc. Toscana Sci. Nat. Pisa, Proc. Verbali Mem.*, **68A**, 23 (1961).

[5] R. Rossi, P. Pino, F. Piacenti, L. Lardicci, and G. Del Bino, *J. Org. Chem.*, **32**, 842 (1967).

[6] (a) The composition assumed for the hydroformylation products of linear butenes in the experiment carried out under CO pressure (7 atm) was 61% *n*-pentanal and 39% 2-methylbutanal. Under these conditions both butene-1 and *cis*- and *trans*-butene-2 give hydroformylation products having the same composition.[6b] It was finally assumed that in the experiment carried out under 75 atm of CO pressure butene-2 was the only olefin formed which, by hydroformylation under the same conditions, gives 71% *n*-pentanal and 29% 2-methylbutanal. Such an assumption was justified by the vpc analysis of the residual gases showing that *cis*- and *trans*-butene-2 was accompanied by only small amounts of butene-1 (<5%). (b) F. Piacenti, P. Pino, R. Lazzaroni, and M. Bianchi, *J. Chem. Soc., C*, 488 (1966).

[7] The ir spectrum of $HCo(CO)_4$ in ethyl ether shows a strong band at 1887 cm^{-1} which should be attributed to the $[Co(CO)_4]^-$ anion [O. Vohler, *Ber.*, **91**, 1235 (1958)] and is missing in hydrocarbon solvents [G. Bor and L. Markó, *Spectrochim. Acta*, **16**, 1105 (1960)].

[8] Prepared as described for analogous acylcobalt carbonyl derivatives: R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **84**, 2499 (1962).

[9] I. Wender, H. W. Sternberg, and M. Orchin, *ibid.*, **75**, 3041 (1953).

[10] R. F. Heck, *ibid.*, **85**, 1460 (1963).

[11] A. Rosenthal and H. J. Koch, *Tetrahedron Lett.*, 871 (1967).

[12] P. Pino, F. Piacenti, M. Bianchi, and R. Lazzaroni, *Chim. Ind.* (Milan), **50**, 106 (1968).