

*Anal.* Calcd for  $C_{13}H_{20}N_2O_8$ : 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.<sup>12a,16</sup> 122°, 141°); uv max (95% EtOH), 372 m $\mu$  ( $\epsilon$  25,500) [lit.<sup>12a</sup> uv max (CHCl<sub>3</sub>), 372 m $\mu$  ( $\epsilon$  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.

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

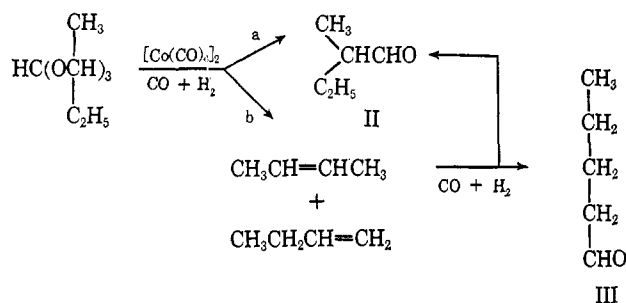
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The synthesis of aldehydes from orthoformic esters, CO and H<sub>2</sub> has been already investigated to determine its possibilities and limitations as a synthetic method<sup>1,2</sup> and a mechanism has been suggested to rationalize its course.<sup>3</sup>

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<sub>2</sub> (Chart I) in the presence of [Co(CO)<sub>4</sub>]<sub>2</sub>.



*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<sup>4,5</sup> and was lower at lower CO pressures.

As previously shown,<sup>2</sup> II is formed both directly from the ortho ester (path a) and by hydroformylation of the butenes formed by the decomposition of I probably

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(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).

via alkylcobalt carbonyls<sup>3</sup> (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.<sup>6</sup> 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 ± 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<sub>N</sub>1 nucleophilic substitution to the saturated carbon atom, as such a mechanism would lead to extensive racemization, and an S<sub>N</sub>2 nucleophilic substitution to the saturated carbon atom is strongly suggested.

To gain evidence on the nature of the nucleophile, HCo(CO)<sub>4</sub> was treated with a large excess of racemic I at 0° under N<sub>2</sub> at atmospheric pressure. In fact, HCo(CO)<sub>4</sub> dissociates in polar solvent giving rise to the formation of the [Co(CO)<sub>4</sub>]<sup>-</sup> anion.<sup>7</sup>

After addition of P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, *sec*-C<sub>4</sub>H<sub>9</sub>COC<sub>2</sub>H<sub>5</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> could be isolated and identified by comparing its ir spectrum with that of an authentic sample.<sup>8</sup>

In another experiment, racemic I was treated with CO and H<sub>2</sub> in the presence of NaCo(CO)<sub>4</sub>. 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)<sub>4</sub>]<sub>2</sub> under reaction conditions is mainly transformed into HCo(CO)<sub>4</sub>,<sup>9</sup> an attractive mechanism for the formation of II through path a involves a nucleophilic attack by the [Co(CO)<sub>4</sub>]<sup>-</sup> anion on the protonated ortho ester (Chart II).

Similar nucleophilic attacks by [Co(CO)<sub>4</sub>]<sup>-</sup> have been suggested in other carbonylations<sup>10</sup> and particularly in the carbonylation of sugar halides occurring with inversion of configuration.<sup>11</sup>

However, taking into account that in some carbonylations HCo(CO)<sub>4</sub> 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,<sup>12</sup> the above scheme (Chart II) should be considered more an attempt to rationalize the experimental results than a proper representation of the reaction mechanism.

(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.<sup>6b</sup> 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)<sub>4</sub> in ethyl ether shows a strong band at 1887 cm<sup>-1</sup> which should be attributed to the [Co(CO)<sub>4</sub>]<sup>-</sup> anion [O. Vohler, *Ber.*, **91**, 1235 (1958)] and is missing in hydrocarbon solvents [G. Bor and L. Markó, *Spectrochim. Acta*, **16**, 1105 (1960)].

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TABLE I  
REACTION<sup>a</sup> OF (+)-TRIS[(S)-1-METHYLPROPOXY]METHANE (I) WITH CARBON MONOXIDE AND HYDROGEN

Expt	P <sub>CO</sub> , atm	Optical purity of ortho ester, %	Equiv of carbonyl compounds/mol of ortho ester, %	Mol of 2-methylbutanal/mol of total aldehyde, %	Mol of <i>n</i> -pentanal/mol of total aldehyde, %
1	75	18.13	83.5	82.2	17.8
2	7	18.38	85.9	71.4	28.6

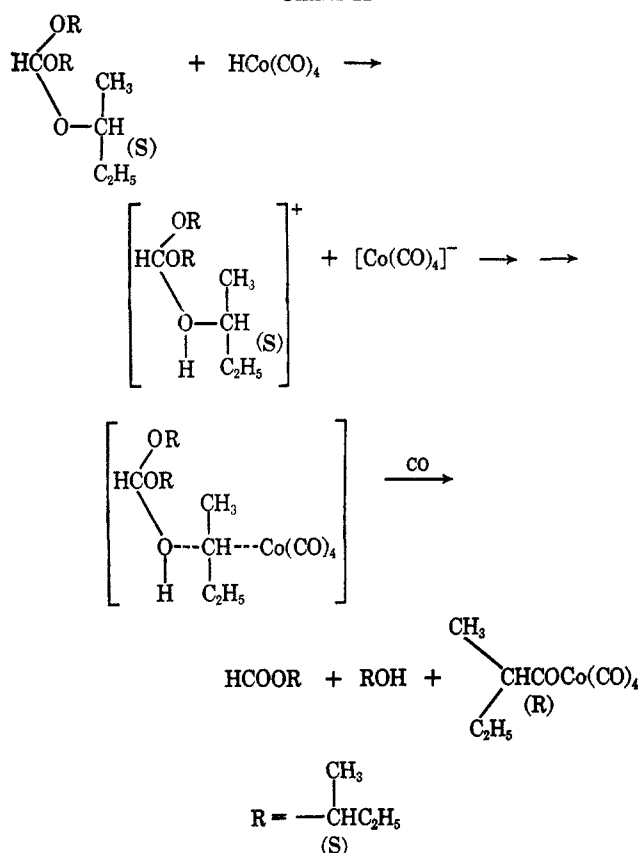
<sup>a</sup> Reaction conditions were 9 g of I, 40 ml of xylene, 0.32 g of [Co(CO)<sub>4</sub>]<sub>2</sub>, a temperature of 90°, and a hydrogen pressure of 75 atm.

TABLE II  
COMPOSITION AND CHARACTERISTICS OF THE ACIDS OBTAINED BY OXIDATION OF THE ALDEHYDES FORMED BY REACTING I WITH CARBON MONOXIDE AND HYDROGEN

Expt	Mol of 2-methylbutanoic acid/mol of C <sub>5</sub> acids, %	Mol of <i>n</i> -pentanoic acid/mol of C <sub>5</sub> acids, %	α <sup>25D</sup> (l = 1), deg	(-)-( <i>R</i> )-2-Methylbutanoic acid optical purity, %	Optical yield— I <sup>a</sup> II <sup>b</sup>
1	73.0	27.0	-1.807	13.47	74.3 93 ± 4
2	72.8	27.2	-1.600	11.96	65.1 99 ± 4

<sup>a</sup> Calculated from the optical purity of (-)-(*R*)-2-methylbutanoic acid formed, with reference to the optical purity of the ortho ester; [α]<sup>25D</sup> max for (-)-(*R*)-2-methylbutanoic acid -19.71°. <sup>b</sup> Calculated considering (1) 2-methylbutanal racemization by heating during the reaction and its oxidation (12 ± 4%) and (2) the presence of racemic 2-methylbutanal due to hydroformylation of butenes.

CHART II



### Experimental Section<sup>13</sup>

(+)-Tris[(S)-1-methylpropoxy]methane (I).—(+)-(*S*)-Butan-2-ol (37.42 g, 0.506 mol) having [α]<sup>25D</sup> +8.402° (optical purity 61.64%<sup>14,15</sup>) was mixed with methyl orthoformate (13.4 g, 0.126 mol) and distillation was started. Methyl alcohol was first separated (11 g), then (+)-(*S*)-butan-2-ol in excess (15 g)

(13) All boiling points are uncorrected. Vpc analysis was performed on a Perkin-Elmer Model F11 instrument equipped with 4-M columns filled either with dinonyl phthalate-sebacic acid on Chromosorb (acidic analysis) or polyethylene glycol (400) monostearate on Chromosorb (aldehydic analysis). Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer; the high-pressure equipment used is the same as we described in previous papers.<sup>5,6</sup>

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and finally 19.6 g of I (67% yield): bp 105° (17 mm); *n*<sup>20D</sup> 1.4143, *d*<sup>25</sup> 0.8638, [α]<sup>25D</sup> +28.40° (61.58% optical purity<sup>16</sup>).

Racemization of (+)-(*S*)-2-Methylbutanal under Reaction Conditions and Subsequent Oxidation to Acid by Ag<sub>2</sub>O.—A solution of (+)-(*S*)-2-methylbutanal<sup>4</sup> (1.6 g) ([α]<sup>25D</sup> +34.00°, optical purity 96.85%, bp 91–92°), 2-butylformate (2 ml), butan-2-ol (1.6 ml), and [Co(CO)<sub>4</sub>]<sub>2</sub> (0.4 g) in xylene (40 ml) was heated at 90° for 3 hr in a 125-ml autoclave under CO and H<sub>2</sub> (1:1, 140 atm).

The solution was then added, at 0°, to an aqueous suspension of Ag<sub>2</sub>O (0.05 mol) prepared from AgNO<sub>3</sub> (17.0 g) and NaOH (8.0 g) in H<sub>2</sub>O (125 ml).

The mixture was then stirred for 3 hr at 0° and 2 hr at 40° and then worked up in the usual manner. After distilling three times, 0.8 g of (+)-(*S*)-2-methylbutanoic acid was recovered, [α]<sup>25D</sup> +16.02° (optical purity 81.33%,<sup>4</sup> racemization 16.0%).

In two other analogous tests racemizations of 8.0 and 13.1% were obtained.

Reaction of I with CO and H<sub>2</sub> in the Presence of [Co(CO)<sub>4</sub>]<sub>2</sub>.—We describe here experiment 1 of Tables I and II. A solution of I (9.16 g, 0.0394 mol; [α]<sup>25D</sup> +8.362°; optical purity 18.13%) and [Co(CO)<sub>4</sub>]<sub>2</sub> (0.32 g) in 40 ml of xylene was introduced by suction into a 125-ml autoclave, then CO and H<sub>2</sub> (1:1) pressure was raised to 120 atm.

The autoclave was heated to 90° and gas absorption commenced. The gas pressure was kept constant during the whole reaction as described in previous papers.<sup>5,6</sup> Gas absorption was complete in 2 hr. After cooling, 41.7 g of liquid reaction mixture was collected. The carbonyl compounds present in the reaction products, determined according to Smith and Mitchell,<sup>17</sup> were 0.033 equiv (yield 83.5%). The ratio between *n*-pentanal and 2-methylbutanal in the crude stage was found to be, by vpc analysis, 17.8:82.2. The aldehydes present in the reaction product were then oxidized to the corresponding acids as described above.

After three distillations, there was recovered a mixture (1.26 g) of *n*-pentanoic and 2-methylbutanoic acids which, by vpc analysis, was shown to contain 27% the former and 73% the latter acid; the rotatory power of this mixture was α<sup>11D</sup> -1.807° (l = 1).

To check the approximation involved in calculating the optical purity of (-)-(*R*)-2-methylbutanoic acid by comparing its α<sup>25D</sup> (l = 1) (homogeneous product) with the α<sup>25D</sup> (l = 1) of the above mixture, the optical rotatory power of a solution of (+)-(*S*)-2-methylbutanoic acid, 69.25% [optical purity 89.25%; α<sup>25D</sup> +16.41° (l = 1)] in *n*-pentanoic acid, 30.75%, was determined, which resulted in an optical rotation of α<sup>25D</sup> +11.21° (l = 1). By assuming, as we have done in our subsequent calculations, that the density of the mixture is equal to that of 2-methylbutanoic acid (0.9329), the optical purity of (+)-(*S*)-2-methylbutanoic acid calculated from the optical rotation of the solution is 88.07 ± 1.4%.

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(17) D. M. Smith and J. Mitchell, Jr., *Anal. Chem.*, **22**, 750 (1950).

**Reaction of Tris[(*RS*)-1-methylpropoxy]methane (IV) with CO and H<sub>2</sub> in the Presence of NaCo(CO)<sub>4</sub>.**—A solution of tris compound IV (14 g) and NaCo(CO)<sub>4</sub> (1.78 g) in butan-2-ol (19.5 ml) was introduced in a 125-ml autoclave and then CO and H<sub>2</sub> (1:1) were added up to 140 atm. The autoclave was heated up to 100° for 3 hr. A pressure drop of 9 atm was noted. After cooling, 29 g of liquid product was collected. The carbonyl compounds present in the reaction products were 0.011 equiv (18.3% conversion). Only traces of unreacted orthoformic ester could be detected.

**Reaction of Tris[(*RS*)-1-methylpropoxy]methane (IV) with HCo(CO)<sub>4</sub>.**—A solution of HCo(CO)<sub>4</sub> (0.4 g, 0.0023 mol) in ethyl ether (5 ml), cooled at 0°, was slowly added, under N<sub>2</sub> and with stirring, to a solution of IV (5.3 g, 0.023 mol) in ethyl ether (5 ml). After standing at 0° for 1 hr, the solution was kept at room temperature for 1 hr and then P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (0.7 g, 0.0027 mol) in ethyl ether was added. After standing for 1 hr the solution was evaporated almost to dryness at 0° under reduced pressure. From the residue, by crystallization from *n*-pentane at -70°, a pale yellow crystalline precipitate was recovered which, by comparing its ir spectrum with that of an authentic sample,<sup>8</sup> was identified as *sec*-C<sub>4</sub>H<sub>9</sub>COCOC(CO)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

**Registry No.**—I, 17159-00-1; carbon monoxide, 630-08-0; [Co(CO)<sub>4</sub>]<sub>2</sub>, 14638-72-3; IV, 17159-01-2.

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### Allenes by Lithium Aluminum Hydride Reduction of Propargyl Derivatives

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Although earlier reports have suggested that both allenes and acetylenes can be products of the lithium aluminum hydride reduction of propargyl or allenyl halides,<sup>2-9</sup> careful studies utilizing gas chromatography, reported recently by Jacobs and coworkers,<sup>3,7</sup> have shown that hydride reduction of either 3-chloro-3-methyl-1-butyne (**1a**) or the corresponding bromo compound **1b** yields 3-methyl-1,2-butadiene but no 3-methyl-1-butyne. Nevertheless, substantial contamination of the allene obtained from the chloro compound **1a** with over-reduced hydrocarbons such as 3-methyl-1-butene, 2-methyl-2-butene, and 2-methylbutane limited the synthetic utility of this process. Although the bromo derivative **1b** was reduced cleanly and in high yield to the desired allene, this starting material was not readily obtained in pure form.<sup>7</sup> The corresponding 1-halo-3-methyl-1,2-butadienes (**2**) were observed to give 3-methyl-1-butyne but no 3-methyl-1,

2-butadiene, thus graphically illustrating that common intermediates are not involved in the reductions of these two related systems. Again, over-reduction was found to be a problem with both the chloro- and bromoallene.



In the present work we have demonstrated that the lithium aluminum hydride reduction of secondary and tertiary propargyl chlorides constitutes a useful synthetic method for the corresponding allenes under modified reaction conditions. Thus, hydride reduction of **1a** in diethyl carbitol cooled in an ice-salt bath, followed by hydrolysis and removal of the volatile product from the reaction mixture by distillation, gave a 47% yield of 3-methyl-1,2-butadiene. This material was homogeneous by glpc and was specifically shown not to be contaminated with the over-reduced products encountered in the earlier work.<sup>3</sup> Furthermore, a similar clean product can be obtained more directly in 29% over-all yield from the corresponding alcohol by hydride reduction of the *crude* product from the preparation of chloride **1a**. Since the yield of purified chloride is only *ca.* 50% and a fractional distillation is avoided, this procedure is the method of choice for preparative purposes.

Under the same conditions hydride reduction of **2b** gave 3-methyl-1-butyne. Although 7% of 3-methyl-1-butene was formed as a by-product in this case, again over-reduction was much less prevalent than found previously.

As a mechanistic probe the above reductions were also performed using lithium aluminum deuteride. Nmr analysis of the 3-methyl-1,2-butadiene thus obtained from **1a** indicated selective and complete deuterium incorporation at one olefinic hydrogen. The mass spectrum confirmed this result by demonstrating the incorporation of a minimum of 94% of one deuterium. Nmr analysis of the 3-methyl-1-butyne obtained by similar reduction of **2b** showed that one deuterium was specifically incorporated at the methine position, as indeed Jacobs and Wilcox had previously demonstrated under their conditions. These reductions imply not only that hydride attack is specific at the terminal acetylene and the disubstituted methylene, respectively, but also that related conversions will provide a useful synthetic method for the preparation of specifically labeled acetylenes and allenes.

The successful reduction of **1a** prompted comparison with a similar sequence utilizing the secondary propargyl alcohol **3a**. Unfortunately no entirely satisfactory method for the clean conversion of **3a** into the corresponding chloride (**3b**) has been developed.<sup>5,10</sup> Phosphorous oxychloride gave a moderate yield of chloride, but this material was an 85:15 mixture of the desired acetylenic compound and the isomeric allene **4**. Redistillation afforded **3b** contaminated by only 7% of **4**, and this material was used for the reduction studies. A variety of other reagents and conditions for preparing the chloride were even less effective in our hands. The standard hydride reduction procedure gave a good yield of 1,2-hexadiene containing about 7%

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