

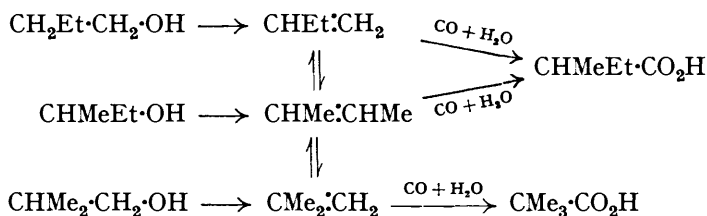
85. *Interaction of Carbon Monoxide and Alcohols. Part III.*  
*Synthesis of Methyleneethylacetic and Pivalic Acids.*

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UNDER conditions identical with those employed in Part II (preceding paper), the reactions between carbon monoxide and *n*-, *sec*-, and *iso*-butyl alcohols have now been examined. In each case, formation of acids took place most readily at 200—210°. The products, which closely resembled those from the propyl alcohols, consisted of an upper layer containing unchanged alcohol, acids, esters, and hydrocarbons, and a lower aqueous layer in which small amounts of acids and unchanged alcohol were dissolved.

The acids from *n*- and *sec*-butyl alcohol were methyleneethylacetic and pivalic (trimethyleneacetic), with a considerable proportion of higher homologues, of which nonoic acids were the chief constituents. The separation of methyleneethylacetic from pivalic acid could only be accomplished after conversion into their methyl esters, whereby it was found that pivalic acid was the major component. On the other hand, *isobutyl* alcohol yielded pivalic and higher acids with but a trace of methyleneethylacetic acid, so that almost pure pivalic acid was obtainable by fractional distillation.

As suggested in Part II (*loc. cit.*), it is again evident that the alcohols are converted into butylenes and butylenic polymerides. With carbon monoxide and steam the former yield five-carbon acids whereas the latter lead to higher acids. The molecular rearrangements involved in converting *n*- and *sec*-butyl alcohol into pivalic acid, and *isobutyl* alcohol into methyleneethylacetic acid must be attributed to butylenic interchange, evidence for which has been provided by Konovalov (*Ber.*, 1880, **13**, 2395), Ipatiev (*Ber.*, 1903, **36**, 1999; 1907, **40**, 1827), Senderens (*Compt. rend.*, 1907, **144**, 1110), and others :



Young and Lucas (*J. Amer. Chem. Soc.*, 1930, **52**, 1964) consider that *isobutylene* is not obtainable from  $\alpha$ - and  $\beta$ -butanol by catalytic dehydration, but under the experimental conditions employed in this research it is evident that, not only is their view incorrect, but *isobutylene* must be the chief dehydration product.

It was always observed that, after use, the catalyst contained metallic copper, evidently produced by reduction of the initial copper phosphate. Since the efficiency was unimpaired, it appeared that copper phosphate might have no promoting action in these experiments. To test this matter, phosphoric acid alone was employed as catalyst in an experiment with *n*-butyl alcohol and carbon monoxide; formation of acids occurred quite readily, and the product was indistinguishable from others obtained by the employment of copper-containing catalysts.

The following carbon balance was obtained :

Carbon introduced, g.		Carbon accounted for, g.	
As <i>n</i> -butanol .....	1000	As unchanged <i>n</i> -butanol .....	437
„ CO .....	62.5	„ hydrocarbons, etc. ....	97
	1062.5	„ acids .....	437.5
		„ butylenes .....	55.5
		Loss.....	35.5
			1062.5

## EXPERIMENTAL.

Except where otherwise mentioned, the experimental conditions and the method of working up the products were as described in Part II. The alcohols were introduced into the vaporiser after addition of 25% by weight of water. Conversion of methyl esters into the corresponding anilides was accomplished by treatment with anilinomagnesium bromide (Hardy, this vol., p. 398).

*n*-Butyl Alcohol and Carbon Monoxide.—(1) *Copper phosphate-phosphoric acid catalyst*. After approx. 2400 g. of *n*-butyl alcohol had been passed through the catalyst at 205–210° during 13 hours, the product, which contained 2243 g. of upper layer (free acid,\* 23.2; total acid,\* 26.3%) and 380 g. of lower layer (free acid,\* 1.6%), furnished 1160 g. of dry butyl alcohol and 115 g. of hydrocarbons, etc. The acids distilled as follows :

B. p. ....	160–169°	169–190°	Residue	Total
Wt. (g.) .....	304	84	190	578

Fractions 1 and 2 were separately converted into methyl esters, and those from the first fraction were fractionally distilled up to 110°, whereupon esters from the second were added and distillation continued :

B. p. ....	99–104°	104–108.5°	108.5–113°	113–125°	Residue
Wt. (g.) .....	245	37.5	1.5	80	19.5

Fraction 1 consisted of methyl pivalate and gave pivalanilide, m. p. 125–125.5° and mixed m. p. with an authentic specimen (m. p. 131°) 126–129°. Fraction 4 was methyl methylethylacetate, and a portion, b. p. 114–117°, gave an anilide, m. p. 103–106°, mixed m. p. with methylethylacetanilide (m. p. 107–108°) 104–107°.

(2) *Phosphoric acid catalyst*. In 6 hours, 749 g. of *n*-butanol were passed through the catalyst at 204–207°; the upper layer of product (C, 58.8; free acid,\* 28.9; total acid,\* 32.9%) weighed 788 g., and the lower layer (C, 4.5; free acid,\* 1.8%) 218 g. From the upper layer (704 g.) were obtained 48.5 g. of hydrocarbons, etc. (C, 78.2; H, 13.0%), and aqueous butanol equivalent, from its carbon content, to 294 g. of dry alcohol. A further quantity (8 g.) of *n*-butyl alcohol was obtained from the lower layer (91 g.). The approximate distribution of the acids was shown by distillation :

B. p. ....	159–170°	170–190°	Residue	Total
Wt. (g.) .....	115	22.5	99.5	237

A quantity of residual acids (b. p. > 190°) was distilled up to 130°/2 mm. and then further to 143°/2 mm., whereupon decomposition commenced. The portion, b. p. < 130°/2 mm., was redistilled under atmospheric pressure with an electrically-heated Dufton column, and the equivalent weights of the fractions were determined by titration (Calc. for C<sub>8</sub>H<sub>17</sub>·CO<sub>2</sub>H : M, 158).

B. p. ....	183—	190—	200—	210—	220—	230—	240—	Residue	130—	Residue
	190°	200°	210°	220°	230°	240°	270°	2	143°/2 mm.	1
Wt., % ...	9.3	4.3	8.3	6.4	4.7	31.6	13.2	5.1	7.0	10.0
M .....	113.5	120	135	150	159	158	177	—	245	—

*sec*-Butyl Alcohol and Carbon Monoxide.—Passage of *sec*-butyl alcohol (ca. 1 kg.) through the catalyst at 200–210° during 6½ hours gave 819 g. of upper layer (Free acid,\* 37.3; total acid,\* 44.3%) and 333 g. of lower layer (Free acid,\* 3.2%). The upper layer (740 g.) contained 214 g. of unchanged alcohol and 46 g. of hydrocarbons, etc. Unchanged alcohol (15 g.) was also obtained from the lower layer (298 g.). The acids were distilled as follows : (1) 160–170°,

\* Calculated on the assumption that its molecular weight is 102.

67.4 g.; (2) 170—190°, 105.3 g.; residue, 105 g.; and the methyl esters from (1) and (2) were then fractionally distilled :

B. p. ....	98—104°	104—109°	109—114°	114—118°	Residue
Wt., % .....	28.8	19.9	17.4	10.5	23.4

The ester of b. p. 99—102° gave an anilide (m. p. 124—126°; mixed m. p. with pivalanilide, 127—129°), and that of b. p. 114—118° gave methylethylacetanilide (m. p. 104—105°; mixed m. p. 105—106°).

*isoButyl Alcohol and Carbon Monoxide.*—*iso*Butyl alcohol (*ca.* 1 kg.) was passed through the catalyst at 215—216° in 6 hours, and produced 1070 g. of upper layer (free acid,\* 22.7; total acid,\* 26.4%) and 234 g. of lower layer (free acid,\* 1.6%). The product (986 g. of upper, and 214 g. of lower layer) gave dry *isobutyl* alcohol (416 g.) and hydrocarbons, etc. (52 g.). Acids were fractionally distilled : (1) 160—164°, 23 g.; (2) 164—166°, 102 g.; (3) 166—180°, 28 g.; (4) residue, 69 g. Fraction (2) solidified and consisted of fairly pure pivalic acid (anilide, m. p. 124—125°; mixed m. p. 125—129°), which melted at 28—30° after drainage in a sintered-glass funnel under reduced pressure. Fractions (1) and (2) were united and converted into methyl esters, which were fractionally distilled :

B. p. ....	99—104°	104—109°	109—114°	114—118°	Residue
Wt., % .....	61.4	20.2	4.5	3.1	10.8

The ester of b. p. 114—118° gave an anilide (m. p. 94—95°; mixed m. p. with methylethylacetanilide, 95—98°).

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