

Treatment of the carbinol with phosphorus trichloride or tribromide gave liquid products which decomposed on distillation and were too low melting to crystallize. The same difficulty was met when thionyl chloride was used in place of phosphorus trichloride.

### Summary

Three new acetylenic carbinols, tripropinylcarbinol, tridonadecynylcarbinol and di-*n*-propylpropinylcarbinol, which contain the group  $-\text{CH}_2-\text{C}\equiv\text{C}-\underset{\text{R}}{\overset{\text{R}}{\text{C}}}-\text{OH}$  have been characterized. Their behavior toward various reagents shows that they do not react in the manner which would be predicted from the knowledge gained previously from the study of closely related acetylenic carbinols containing the group  $\text{R}_3\text{C}-\text{C}\equiv\text{C}-\underset{\text{R}}{\overset{\text{R}}{\text{C}}}-\text{OH}$ .

URBANA, ILLINOIS

RECEIVED MAY 20, 1933

PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION NO. 43 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

## The Direct Carboxylation of Carbon Compounds. II

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In a recent study of the equilibrium  $\text{C}_6\text{H}_6\text{CO}_2\text{H} \rightleftharpoons \text{C}_6\text{H}_6 + \text{CO}_2$  it was found that benzene was carboxylated directly by carbon dioxide.<sup>1</sup> Temperatures of about 300° and pressures of about 30 atmospheres were used and the catalyst was of the Zn-Cu-Cr oxide type. Since the yield of acid product as well as the rate of the reaction was quite low, we have continued the search for a more active catalyst. In addition we have studied the direct carboxylation of a variety of compounds.

The experiments were all conducted in glass bomb tubes having a volume of 160 to 200 cc. Pressures of 20 to 30 atmospheres were obtained by introducing into each tube before sealing 0.1 mole of solid carbon dioxide. The tubes were heated for eight hours in a Carius furnace at the temperatures recorded in the table for each specific substance.

A catalyst was found to be quite essential for the carboxylation under the conditions given. The catalyst mentioned in the first paper was replaced by a similar mixture of oxides, but supported on asbestos. This change increased the activity of the catalyst based on the weight of metal oxides in the mixture. It was made by mixing thoroughly the well washed moist hydroxides obtained from 99 g. of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 93.5 g. of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  by precipitation with ammonium hydroxide, with 7.7 g. of chromic oxide and 40 g. of asbestos. After drying the mixture was ignited to convert the hydroxides to oxides. This type of catalyst was found to decrease in activity with use. Upon using the same catalyst over

(1) Kinney and Langlois, *THIS JOURNAL*, **53**, 2189 (1931).

for a second and a third time the yield of acid from toluene dropped from 0.36 to 0.15% and to 0.05% for the third run.

In attempting to avoid some of these difficulties a Ni-Co oxide catalyst was developed that was of approximately equal activity. It was made by dissolving 20 g. of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 24 g. of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in a small amount of water and mixing the solution with 15 g. of dry asbestos fiber. After drying the asbestos was ignited until no more oxides of nitrogen were evolved, when the catalyst was ready for use. This catalyst induced a yield of 0.33% of crude acid product from toluene as compared with 0.36% using the Zn-Cu-Cr oxide catalyst, consequently the latter catalyst was used in all the experiments recorded in the table.

After heating the various substances with carbon dioxide, two methods were used to isolate the products of carboxylation depending upon whether the substance was phenolic or not. In case the substance was not phenolic the contents of the tube were extracted with hot half normal potassium hydroxide. The acids were liberated with dilute sulfuric acid and extracted from the solution with several small portions of ether. The ether extract was dried with anhydrous sodium sulfate, filtered and the ether evaporated. The residue of crude acid was then treated as described below.

The reaction products from the phenolic compounds were extracted with a 10% sodium bicarbonate solution that had just been saturated with carbon dioxide. Since carboxylic acids displace carbonic acid from its salts while phenols do not it was possible to extract the phenolic compounds from the bicarbonate solution by repeated ether extractions. After making at least five such extractions with ether the bicarbonate solution was boiled with activated carbon and acidified with dilute sulfuric acid. The liberated acids were next extracted by several portions of ether, and isolated as described for the product from the non-phenolic substances above.

The crude acid products from toluene, anisole, nitrobenzene and styrene were purified by sublimation. In all other cases, the melting points and mixed melting points recorded in the table were obtained with the crude product.

The yields given in the table may not be the maximum obtainable since only two

TABLE

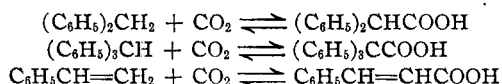
Substance used, g.	Temp., °C.	Calcd. press. in atm.	Yield of acid prod., %	M. p., °C.	Mixed m. p., °C.	M. p. of acid used for mixed m. p., °C.	Name of acid used for mixed m. p.
Toluene (2)	300-310		0.36	120-130	140-150	176	<i>p</i> -Toluic
Diphenylmethane (2) (a)	158-160	21.5	.19	140-143	143	146	Diphenylacetic
(b)	238-243	21.0	.44	141-142	143-144	146	
Triphenylmethane (2)	158-160	24.0	.33	259-260 dec.	260 dec.	263 dec.	Triphenylacetic
Styrene (3)	295-305	33.0	.28	120-121	129-129.5	133	Cinnamic
Phenol (2) (a)	115-117		Trace				
(b)	144-145	16.0	Trace				
(c)	205-208		None				
Anisole (2) (a)	218-222		Trace				
(b)	238-243	26.0	0.24	145-150	154-163	177	Anisic
Bromobenzene (6)	295-300	28.0	.14	220-222	238-239	251	<i>p</i> -Bromobenzoic
Dimethylaniline (3)	218-222	21.5	.10	209-210	213-214	230	<i>p</i> -Dimethyl-aminobenzoic
Nitrobenzene (3)	290-300	26.5	.21	220-222	230-230.5	237	<i>p</i> -Nitrobenzoic
Catechol (2) (a)	124-125	20.0	.64	117-124 dec.	135-148 dec.	197 dec.	2,3-Dihydroxybenzoic
(b)	170-173	19.0	Trace				
Resorcinol (1)	115-120	22.0	10.60	115-123 dec.	158-167 dec.	201 dec.	2,4-Dihydroxybenzoic
Quinol (2)	115-120	25.0	0.39	145-154 dec.	171-173 dec.	195 dec.	2,5-Dihydroxybenzoic

or three variations in temperature were made at most for any one substance. However the yields given were checked by duplicate runs. In addition, eight hours may be insufficient for the reaction to come to equilibrium as the rate of the reaction is probably low.

The melting point of the acid product in some cases was quite low compared to that of the pure acid used for comparison. For example the sublimed acid product from toluene melted 40–50° lower than the pure *p*-toluic acid used for the mixed melting point. The low melting point was probably due to the presence of a small amount of benzoic acid coming from the oxidation of the toluene by the oxide catalyst. This was verified by heating toluene with the catalyst in the absence of carbon dioxide, whereby a trace, compared to the yield of acid obtained when carbon dioxide was present, of a sublimable acid was obtained. If the impurity in the product from toluene was benzoic acid a study of mixed melting points showed that the sublimed acid contained only about 5% benzoic acid.

The products obtained from the dihydroxybenzenes were also very low melting. Again it appeared likely that the impurities were oxidation products as evidenced by their high color. In any event the impurity could not have been the unreacted phenolic compound as the method employed to separate artificial mixtures of the phenols and the corresponding carboxylated product was highly satisfactory. No explanation for the large yield from resorcinol can be offered at this time.

The carboxylation of diphenylmethane, triphenylmethane and styrene were of particular interest because of the carboxylation of aliphatic carbon-hydrogen bonds.



The products of these three reactions were relatively pure and could be identified without trouble.

Likewise, bromobenzene, anisole, dimethylaniline and nitrobenzene gave fairly pure para carboxylation products considering the probability of simultaneous carboxylation in other positions.

In all cases studied thus far, with the possible exception of phenol, carboxylation has occurred. The reaction takes place with both aromatic and aliphatic carbon to hydrogen bonds; and, although the reaction is highly reversible with the position of equilibrium far on the side of decarboxylation, the reaction appears to be of a quite general nature.

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RECEIVED MAY 22, 1933  
PUBLISHED SEPTEMBER 5, 1933