Reactive Cleavage of *tert*-Alkyl Aromatic Hydrocarbons by Carbon Monoxide and Strong Acids

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The reaction of carbon monoxide with *tert*-alkyl aromatic hydrocarbons has been studied. High yields of α,α'-dialkyl substituted carboxylic acids are produced by cleavage and reaction of the *tert*-alkyl fragment with carbon monoxide.

The reaction of olefins with carbon monoxide and water to produce carboxylic acids has been studied extensively by Koch and co-workers.[4,5] The carbonylation goes readily at near room temperature under moderate carbon monoxide pressures in the presence of strong acid catalysts. Hydrolysis of the intermediate product–catalyst complex results in high yields of carboxylic acids. Friedman and Cotton[6] recently published a work on carbonylation using anhydrous hydrogen fluoride as catalyst. During the course of this study they showed that *tert*-butylbenzene undergoes reactive cleavage in the presence of hydrogen fluoride and carbon monoxide to produce moderate yields of benzene and trimethylacetic acid. The reactive cleavage of *tert*-alkyl aromatic hydrocarbons under carbonylation conditions using boron trifluoride monohydrate as catalyst has been studied in more detail in this laboratory. High yields of the aliphatic acids expected from addition of carbon monoxide to the tertiary carbonium ions resulting from alkyl group cleavage were produced.

When catalyst is used in molar excess, yields approach the theoretical. Results of carbonylation of selected *tert*-alkyl aromatic hydrocarbons using a boron trifluoride monohydrate/aromatic hydrocarbon ratio of 2 are shown in Table I. It is seen that even under these relatively mild conditions conversions are excellent and selectivities for the expected aliphatic acids and the cleaved aromatic hydrocarbons are high. Of the *tert*-alkyl aromatic hydrocarbons studied, it is apparent that 1,3-dimethyl-5-*tert*-butylbenzene gives the highest conversions and that *tert*-pentyl aromatics were converted to a lesser extent than the *tert*-butyl homologs.

TABLE I

CARBONYLATION OF *tert*-ALKYL AROMATIC HYDROCARBONS

Conditions: CO pressure 500 p.s.i.g.
Temperature 25°
Reaction time 2 hr.
$BF_3 \cdot H_2O$/hydrocarbon 2.0 (M)

Expt. no.	Hydrocarbon	Hydrocarbon converted, %	Yield of acid[a]	Yield of parent hydrocarbon[a]
1	1,3-Dimethyl-5-*tert*-butylbenzene	93.0	89.5	98.4[b]
2	1,3-Dimethyl-5-*tert*-pentylbenzene	72.2	97.5	99.7[b]
3	1-Methyl-5-*tert*-pentylbenzene	74.9	97.9	99.7[c]
4	*tert*-Butylbenzene	46.3	78.9	95.7[d]

[a] Mole % on aromatic converted. [b] *meta*-Xylene. [c] Toluene. [d] Benzene.

Lowering the catalyst to hydrocarbon ratio to one reduced conversions. This effect is shown in Table II. It is apparent that a molar excess of catalyst over hydrocarbon is required for high conversions. Since catalyst is tied up as a complex with the carbonylation product, the excess acid is likely necessary to cause cleavage to proceed to near completion; alkyl group cleavage is likely necessary before carbonylation can occur.

TABLE II

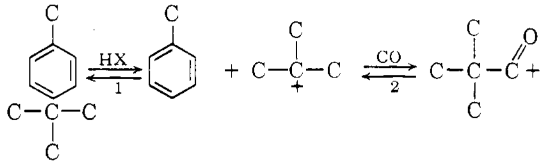
CARBONYLATION OF 1,3-DIMETHYL-5-*tert*-BUTYLBENZENE

Conditions: CO pressure 500 p.s.i.g.
Temperature 25°
Reaction time 2 hr.

Expt. no.	1	5	6
$BF_3 \cdot H_2O$/hydrocarbon (M)	2.0	1.0	0.5
Hydrocarbon converted	93.0	58.6	30.0
Yield of trimethylacetic acid[a]	89.5	97.9	91.7
Yield of *meta*-xylene[a]	98.4	97.0	92.6

[a] Mole % on hydrocarbon reacting.

The high selectivity of the carbonylation of *tert*-alkyl aromatic hydrocarbons is believed to be due to the alkylation–dealkylation equilibrium as illustrated with *tert*-butyltoluene. Since the equilibrium for reaction 1 lies far to the left under conditions employed in this study, it is apparent that *tert*-butyl ions are fed into the system only at the rate that they are consumed by the carbonylation reaction. Polymerization, which is a major side reaction in carbonylation of branched olefins, is not significant here since the carbonium ion concentration is regulated by the position of equilibrium 1. For this reason maintenance of a low olefin or *tert*-alkyl ion concentration results in high selectivities for acid formation.



To illustrate this, a series of runs was made in which carbonylation of a *tert*-alkyl aromatic, an isoölefin in presence of an aromatic, and an isoölefin alone were compared using a catalyst to alkyl group ratio of one. In Table III the yields of trimethylacetic acid produced

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(4) H. Koch, *Riv. Combust.*, **10**, 77 (1956); *Brennstoff-Chem.*, **36**, 321 (1956).

(5) H. Koch, U. S. Patent 2,831,877 (April 22, 1958); Belgian Patent 518,682 (March 4, 1955).

(6) B. S. Friedman and S. M. Cotton, *J. Org. Chem.*, **27**, 481 (1962).

TABLE III

EFFECT OF *tert*-BUTYL SOURCE

Conditions: CO pressure 500 p.s.i.g.
Temperature 25°
Time 2 hr.

Expt. no.	5	7	8
Hydrocarbon charged (moles)			
1,3-Dimethyl-5-*tert*-butylbenzene	4.01	...	...
meta-Xylene	...	3.86	...
2-Methylpropene	...	3.80	3.89
$BF_3 \cdot H_2O$ charged (moles)	4.00	3.80	3.89
tert-Butyl groups consumed (mole %)[a]	58.6	61.3	100.0
Selectivity for trimethylacetic acid[b]	97.9	49.7	36.5
1,3-Dimethyl-5-*tert*-butylbenzene recovered[a] (mole %)	41.4[c]	11.6[d]	...

[a] That reacting to form products other than 1,3-dimethyl-5-*tert*-butylbenzene. [b] Calculated on *tert*-butyl groups reacting as in *a*. [c] Unchanged. [d] Formed by reaction.

by carbonylation of 1,3-dimethyl-5-*tert*-butylbenzene are compared with those produced by direct carbonylation of 2-methylpropene alone and in the presence of *meta*-xylene. In the case of the latter two runs the olefin was fed slowly into the reaction vessel containing the other reactants in order to minimize polymerization, whereas the 1,3-dimethyl-5-*tert*-butylbenzene was all charged at once. The *tert*-alkyl aromatic hydrocarbon gave higher yields of acid than either the olefin with *meta*-xylene or the olefin alone. In the latter cases the 2-methylpropene not going to acid was largely lost to polymer, while with 1,3-dimethyl-5-*tert*-butylbenzene the *tert*-butyl groups not converted to carboxylic acid were retained on the aromatic ring.

Several catalysts other than boron trifluoride monohydrate were tested for this reaction but were found to be ineffective. These included phosphoric acid, sulfuric acid, and methanesulfonic acid. Although anhydrous hydrogen fluoride was not tried, it would be expected to be an effective catalyst in light of the paper by Friedman and Cotton.

Carbonylation of isopropylbenzene was attempted using boron bifluoride monohydrate catalyst, under the conditions of Table I, but not even the odor of isobutyric acid was detectable. Friedman and Cotton were equally unsuccessful in carbonylation of isopropylbenzene in the presence of hydrofluoric acid. This is likely due to the failure of the isopropyl group to cleave under the conditions used.

Due to the specificity of this reaction for *tert*-alkyl groups, it may find utility not only as a method for synthesis of acids, but also as a degradative method of structure determination.

Experimental

Catalysts and Reactants.—The boron trifluoride monohydrate catalyst was prepared by saturating deionized water with anhydrous boron trifluoride at about room temperature as previously described.[7] The carbon monoxide used was a commercial product of the Matheson Company.

1,3-Dimethyl-5-*tert*-butylbenzene was prepared by alkylating *meta*-xylene (95%) with technical grade (98%) diisobutylene (Petro-Tex Chemical Co.) at 30° using boron trifluoride monohydrate as catalyst. The alkylate product was separated by fractionation using a 1 in. × 4 ft. Podbielniak Hypercal column at a 20 to 1 reflux ratio. Analysis by gas chromatography indicated a purity of 98.9% 1,3-dimethyl-5-*tert*-butylbenzene with 0.7% *para*-*tert*-butylethylbenzene and 0.4% *tert*-butyl-*ortho*-xylene as the main impurities.

The *tert*-pentyl aromatics were prepared by alkylating the parent aromatic with 2-chloro-2-methylbutane using an aluminum chloride catalyst and fractionation as described above.

Pure grade (99 mole % minimum) isopropylbenzene and pure grade *tert*-butylbenzene from Phillips Petroleum Co. were used as received.

Experimental Procedure.—All experimental work was carried out in a 2-l. stainless steel autoclave. In each experiment 4 moles of *tert*-alkyl aromatic was charged and sufficient catalyst added to give the desired catalyst/hydrocarbon mole ratio. In a typical experiment 343 g. (4 moles) of catalyst and 649 g. (4 moles) of 1,3-dimethyl-5-*tert*-butylbenzene were charged to the reactor. Carbon monoxide was added to a total reactor pressure of 500 p.s.i.g. at 25° and stirring was started. At the end of the run the system was allowed to settle and the carbon monoxide was vented through a Dry Ice trap. The contents of the reactor were drained into a tared flask and weighed. Water (500 ml.) was added with stirring to the product–catalyst mixture with the temperature held below 25°. The aqueous phase, which contained no significant quantity of acid, was separated and discarded. The organic phase was made basic with 2 *N* sodium hydroxide. The phases were separated and the aqueous portion was extracted with 500 ml. of *para*-xylene, and then acidifiedwith dilute hydrochloric acid until a pH of less than 2 was reached. The carboxylic acid, which formed a separate liquid layer, was separated by means of a separatory funnel. The aqueous layer was extracted with two 500-ml. portions of benzene and the extracts were added to the trimethylacetic acid product previously separated. The mixture was distilled to 125° overhead on a simple one-plate column. The purity of the product, in this example 97%, was determined by acid number.

Experiments in which isobutylene was carbonylated were made as described above with the isobutylene being charged at a constant rate throughout the run by means of a Ruska pump.

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(7) R. J. Lee, H. M. Knight, and J. T. Kelly, *Ind. Eng. Chem.*, **50**, 1001 (1958).