alcohol, catechol, pyrrole, heptaldehyde, *n*-octene-1, naphthalene, and 1,4-diazabicyclo[2.2.2]octane using the technique and reaction conditions described above for reaction with hydrazobenzene. In each case no pyridine could be detected and only unchanged starting materials could be isolated.

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[CONTRIBUTION FROM SINCLAIR RESEARCH, INC.]

Hydrogen Fluoride–Catalyzed Reactions of Hydrocarbons with Carbon Monoxide

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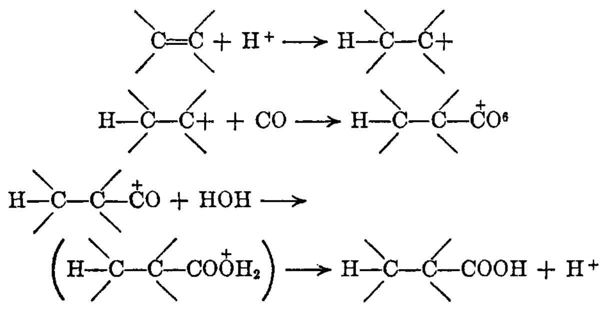
Hydrogen fluoride catalyzes the condensation of olefins with carbon monoxide at room temperature to form acyl compounds. If an alkylatable hydrocarbon such as an isoparaffin or a branched naphthene, R'H, is used as a solvent for this condensation, the solvent undergoes a hydride transfer reaction with the olefin-derived carbonium ion, resulting in a new cation, R'^+. This cation reacts with carbon monoxide to form an acid, R'COOH (after hydrolysis). Hydride transfer also occurs between an acyl fluoride, RCOF, and a branched hydrocarbon *via* decarbonylation and formation of the carbonium ion, R^+. Use of *cis*-decalin as a solvent leads to formation of decalin-9-carboxylic acid, but *trans*-decalin is substantially unaffected. Carboxylic acid solvents containing a tertiary hydrogen do not undergo the hydride transfer reaction, thus ruling out this route to dicarboxylic acids. Hydrogen fluoride does not promote the acylation of benzene or toluene by pivalyl fluoride, but instead produces *t*-butyl derivatives of these aromatics. Treatment of *t*-butylbenzene with carbon monoxide yields pivalyl fluoride. Cumene does not form isobutyryl fluoride. The mechanism of these reactions is discussed.

Some years ago Simons and Werner[1] reported that certain alcohols and alkyl halides condense with carbon monoxide at about 160° in the presence of hydrogen fluoride to form organic acids.

More recently, H. Koch and co-workers have shown that olefins[2,3,5] and alcohols[4,5] condense quite readily at room temperatures and moderate pressures with carbon monoxide in the presence of sulfuric acid to produce (after hydrolysis) good yields of organic acids. They frequently employed formic acid as the source for carbon monoxide. Koch[4] suggested the following mechanism:



Stork and Bersohn[7] and Pincock, Grigat, and Bartlett[8] have found Koch's reaction to be a remarkably smooth synthetic method for complex tertiary acids, in some instances with a high degree of stereospecificity. Koch as well as Bartlett,[8] Meinwald[9] and Lundeen[10] have shown that skeletal and *cis-trans* isomerization may occur, but these reactions often afford excellent yields of the favored isomer. Roe and Swern[11] determined optimum conditions for preparing polycarboxylic acids from oleic, linoleic, and other unsaturated acids.

Although anhydrous hydrogen fluoride[3] and monohydroxyfluoboric acid[12] have been mentioned as catalysts for this reaction of olefin with carbon monoxide, the data for the former are very sparse. We have employed anhydrous hydrogen fluoride as catalyst for the reaction of various hydrocarbons with carbon monoxide,[13] and wish to record some of our findings.

Alkanes and cycloalkanes. In recent papers Wolfgang and Koch[14] reported the synthesis of carboxylic acids from saturated hydrocarbons *via* a hydride-transfer reaction. These authors found that concurrent contact of (a) an olefin or alcohol, with (b) an isoparaffin or a naphthene, and (c) carbon monoxide or formic acid, in the presence of

(1) J. H. Simons and A. C. Werner, *J. Am. Chem. Soc.*, **64,** 1356 (1942).
(2) H. Koch, *Riv. Combustibili*, **10,** 77 (1956); *Brenn. Chemie*, **36,** 321 (1955).
(3) H. Koch, U. S. Patent **2,831,877** (April 22, 1958); Belgium Patent **518,682** (March 4, 1955).
(4) H. Koch, *Fette und Seifen*, **59,** 493 (1957).
(5) (a) H. Koch and W. Haaf, *Angew. Chem.*, **70,** 311 (1958); (b) *Ann.*, **618,** 251 (1958).
(6) This may be written: $R^+ + \bar{C}{\equiv}\overset{+}{O} \longrightarrow R{-}C{\equiv}O^+ \longleftrightarrow R\overset{+}{C}{=}O$. See refs. 9 and 11.
(7) G. Stork and M. Bersohn, *J. Am. Chem. Soc.*, **82,** 1261 (1960).
(8) R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Am. Chem. Soc.*, **81,** 6332 (1959).
(9) J. E. Meinwald, H. C. Hwang, D. Christman, and A. P. Wolf, *J. Am. Chem. Soc.*, **82,** 484 (1960).
(10) A. Lundeen, *J. Am. Chem. Soc.*, **82,** 3228 (1960).
(11) E. T. Roe and D. Swern, *J. Am. Oil Chem. Soc.*, **37,** 661 (1960).
(12) H. Koch and W. Huisken, U. S. Patent **2,876,241** (March 3, 1959).
(13) B. S. Friedman and S. M. Cotton, U. S. Patent **2,975,199** (March 14, 1961); *J. Org. Chem.*, **26,** 3751 (1961).
(14) H. Wolfgang and H. Koch, *Ann.*, **638,** 122 (1960); *Angew. Chemie*, **72,** 628 (1960).

concentrated sulfuric acid, will produce good yields of acid derived from the saturated hydrocarbon, as well as the acids normally derived from the olefin or alcohol. Thus from *t*-butyl alcohol and methylcyclohexane they produced 72% of 1-methylcyclohexanecarboxylic acid, as well as 16% of pivalic acid.

Earlier, patents were issued to A. Schneider[15] on the production of acids from branched paraffins, branched naphthenes, and alkylbenzenes by treatment with olefin-forming compounds and carbon monoxide. Little experimental data were given and no mention made of the concurrent formation of acids from the olefin or olefin-forming reactant.

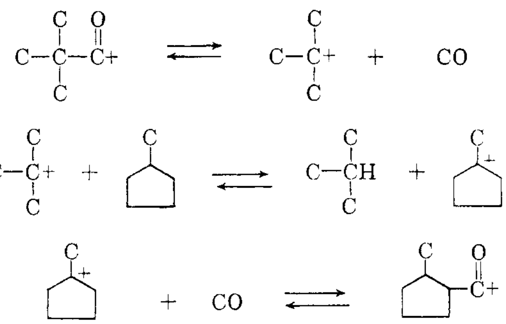
Our results (Table I) with the exchange reaction involving olefins and branched paraffins or branched naphthenes were similar to those obtained by Wolfgang and Koch. However, hydrogen fluoride afforded somewhat lower yields of acids than they obtained with sulfuric acid. This may not apply to hydride transfer reactions involving tertiary halides, since hydrogen fluoride gave a much higher ratio of 1-methylcyclohexane(MCH)carboxylic acid to pivalic acid in the *t*-RCl/MCH/CO reaction than did sulfuric acid (expts. 4 and 5).

We obtained evidence for only a minor amount of hydride transfer in reactions involving the secondary hydrogens of *un*branched paraffins or *un*branched cycloparaffins (expt. 6), whereas with sulfuric acid as catalyst they obtained 19% of exchange acids from cyclohexane and 3% from *n*-hexane. These are striking results in view of the statement[16] that "Although hydride transfers involving secondary alkyl cations take place in aluminum halide systems, they have not been reported for sulfuric acid . . . "

In the alkylbenzene/olefin/carbon monoxide reaction we likewise failed to find the products claimed by Schneider,[15] namely, phenyl-substituted acids (expts. 11 and 12). Hydride transfer did occur as evidenced by the formation of 2-methylpropane in the reaction of 2-methylpropene, *p*-cymene, and carbon monoxide (expt. 11), but here the hydride exchange reaction led to formation of indanes such as 1,3,3,6-tetramethyl-1-*p*-tolylindane[17] and 1,1,3,3,6-pentamethylindane.[18] *p*-Cymene, *t*-butyl chloride, and carbon monoxide (expt. 12) gave the same results. The absence of α,α'-dimethyl-*p*-tolylacetic acid may be explained as follows: The intermediate cation (*A*)—*p*-CH_3-C_6H_4-$\overset{+}{C}(CH_3)_2$—reacts readily with an olefin to form stable indanes. This olefin may consist of *p*-isopropenyltoluene,[17,19] derived from (*A*) by loss of proton, or it may be the incoming olefin, *e.g.*, 2-methylpropene.[18] Cation (*A*) may also react with carbon monoxide to form an acyl cation, but the latter is in equilibrium with (*A*) which is apparently drained off to form the stable indanes.

By treating *trans*-decalin with *t*- or *sec*-butyl-alcohol in the presence of formic acid/sulfuric acid, Wolfgang and Koch obtained 5 to 8% of *cis*/*trans*-decalin-9-carboxylic acid. Though none of the decalin acid resulted from the hydrogen fluoride catalyzed reaction of *trans*-decalin with 2-methylpropene (expt. 9) or with *t*-butyl chloride (expt. 10), we were able to obtain a 10% yield by treating *cis*-decalin with *t*-butyl chloride (expt. 8). Our results are in accord with the greater resistance reported[20] for *trans*-decalin in the aluminum chloride–catalyzed hydrogen transfer reaction with *t*-butyl chloride to yield 9-chlorodecalin.

We have found that an acyl fluoride will also induce reaction of a branched paraffin or cycloparaffin with carbon monoxide. Thus when a preformed condensation product of methylpropene with excess carbon monoxide and hydrogen fluoride was treated at 25° with five moles of methylcyclopentane, a 37% yield of 1-methylcyclopentanecarboxylic acid was formed (after hydrolysis). This reaction probably proceeds *via* decarbonylation (a), followed by hydride transfer (b) and subsequent carbonylation (c):



(a)

(b)

(c)

2-Methylpropane, as required by Equation (b), was produced in an amount roughly equivalent to the 1-methylcyclopentanecarboxylic acid. About one third of the original acyl ion was isolated as pivalic acid.

Others have observed decarbonylation-recarbonylation reactions similar to (a) and (c) when they treated tertiary acids with sulfuric acid.[8–10]

Formation of the methylcyclopentyl cation *via* direct reaction (d) of the pivalolyl ion with methylcyclopentane is doubtful since reduction products[21]

(15) A. Schneider, U. S. Patents **2,864,858** and **2,864,859** (Dec. 16, 1958).

(16) N. C. Deno, H. J. Peterson, and G. S. Saines, *Chem. Revs.* **60**, 7 (1960).

(17) V. N. Ipatieff, H. Pines, and R. C. Olberg [*J. Am. Chem. Soc.*, **70**, 2123 (1948)] obtained this indane by alkylating *p*-cymene with 2-methylpropene and other branched olefins.

(18) M. J. Schlatter obtained this indane by treating *p*-cymene with 2-methylpropene; Div. of Petrol. Chem. 129th Meeting, ACS, Dallas, Tex., April 1956, "Chemicals from Petroleum," Preprints, p. 77.

(19) A. T. Coscis, J. T. Penniston, and J. C. Petropoulos, *J. Org. Chem.*, **26**, 1398 (1961).

(20) F. E. Condon, U. S. Patent **2,629,748** (Feb. 24, 1953).

(21) G. Baddeley and E. J. Wrench, *J. Chem. Soc.*, 1324 (1959).

TABLE I

BRANCHED PARAFFINS, BRANCHED NAPHTHENES, AND CYMENE

Expt. No.	Saturate[a] (Moles)[b]	Olefin or RCl (Moles)	Time[c]		Carbon Monoxide Press. p.s.i.g.[d]	Carbon Monoxide Moles consumed	HF Catalyst, Moles	Temp.	Acid Formed	Moles	i-C_4H_{10}, Moles
1	2-Methylpropane 3.6	C_3H_6 1.07	20	10	870–740	0.6	20.2	25	Isobutyric	0.054	0.1[e]
									Pivalic	0.05	
2	MCP 5	C_3H_6 2	20	34	840–575	1.1	15.8	32	Isobutyric	0.43	e, f
									1-MCP-Carboxylic	0.24	
3a	2,3-DMB 5	i-C_4H_8 2	22	38	180–30	2.0	10.35	20	Pivalic	0.69	0.27
									2,2,3-Trimethylbutanoic	0.86	
3b	2,3-DMB 5	i-C_4H_8 5	122	13	280–100	4.3	10.5	25	Pivalic	1.14	1.33
									2,2,3-Trimethylbutanoic	1.29	
									C_9 Acid	0.3	
									C_{13} Acid	0.3	
4	MCH 4.9	t-BuCl 2	16	44	325–170	1.5	12.8	20	Pivalic	0.5	0.6
									1-MCH-Carboxylic	0.58	
5	MCH 5	t-BuCl 2	195		325–250	f	4.7[g]	25	Pivalic	0.68	0.41
									1-MCH-Carboxylic	0.24	
6	CH 2.5, nC_5 2.5	t-BuCl 2	16	104	280	f	10.7	20	Pivalic	f	0.03
7	1,4-DMCH 5.7	i-C_4H_8 1.23	30	20	880–720	f	12.4	30	Pivalic	0.1	0.5
									1,4-DMCH-Carboxylic	0.39	
									Other Acids	(41g)	
8	*cis*-Decalin 4	t-BuCl 2	24	38	270–200	0.6	10.5	20	Pivalic	0.41	0.84
									Decalin Carboxylic	0.2	
9	*trans*-Decalin 4	i-C_4H_8 2.05	21	18	430–210	2.0	10.3	15	Pivalic	1.47	0.02
									(None from Decalin)		
									Higher Acids	(25g)	
10	*trans*-Decalin 3.62	t-BuCl 3.85	83	52	500–300	2.7	10.45	25	Pivalic	2.15	0.01
									(None from Decalin)		
11	p-Cymene 3	iC_4H_8 2	23	10	175–125	0.6	11.2	20	Pivalic	0.69	0.38[h]
12	p-Cymene 3.75	t-BuCl 1	10	30	730–635	f	10.5	25	Pivalic	0.57	0.28[h]

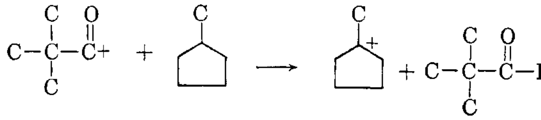
[a] DMB = dimethylbutane, MCP = methylcyclopentane; MCH = methylcyclohexane; CH = cyclohexane; nC_5 = n-pentane; 1,4-DMCH = 1,4-dimethylcyclohexane. [b] Initially present. [c] Minutes to add; minutes additional stirring. [d] Range. [e] Propane. [f] Not determined. [g] 96% sulfuric acid. [h] Resulting largely from formation of 1,1,3,3,6-pentamethylindane[18] and 1,3,3,6-tetramethyl-1-p-tolylindane[17] which were shown to be present by mass spectroscopy and gas-liquid chromatography.

TABLE II

REACTION WITH BRANCHED ACIDS AND ACYL FLUORIDES

Expt. No.	Substrate[a] (Moles)	Methylpropene, Moles	Carbon Monoxide Pressure[b]	Carbon Monoxide Moles[c]	HF, Moles	Temp.	Time, Min.[d]	i-C_4H_{10} Evolved
13	2-C_2H_5-4-Methyl-pentanoic acid[e] (2.45)	5.35	275–165	3.58	15.5	28	40/35	Trace
14	1,4-Dimethyl-CH-carboxylic acid (0.22)	0.32	730–530	[f]	5	27–32	15/30	None
15	C_{10} Acyl fluoride (4) (derived from C_3H_6 trimer)	0.86	560	[f]	12	24–29	15/30	1 g.
16	C_{13} Acyl fluoride (3) (derived from C_3H_6 tetramer)	0.53	600–540	[f]	11.5	28	15/30	0.5 g.

[a] CH = cyclohexane. [b] Range, p.s.i.g. [c] Absorbed, determined by gain in weight. [d] Minutes to add olefin/minutes additional stirring. [e] Eastman Chemical Products, Inc. [f] Not determined.



(d)

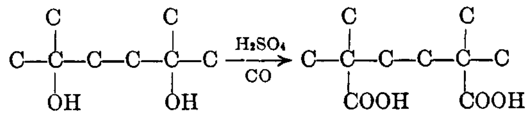
such as pivaldehyde, or carbonyl other than organic acid, were not found.

Branched acids (*Table II*). An attempt was made to introduce a second carboxyl group into an acid which contains a tertiary hydrogen potentially available for the hydrogen transfer reaction. We experienced the same lack of success with the hydrogen fluoride catalyst as did Wolfgang and Koch in most instances with sulfuric acid. For example, when 2-ethyl-4-methylpentanoic was used as solvent for the reaction of 2-methylpropene with carbon monoxide (expt. 13), no 2-methylpropane was formed indicating nonoccurrence of the desired hydrogen transfer reaction involving the tertiary hydrogen on either the alpha or gamma carbon atoms. A similar test made with 1,4-dimethylcyclohexanecarboxylic acid (expt. 14) also showed no evidence of hydrogen transfer further corroborating Wolfgang and Koch. However, they did succeed in producing a 6% yield of C_{14} dibasic acid by treating a highly branched C_{13} acid (from propylene tetramer) with t-butyl alcohol in the presence of sulfuric acid. We found that the branched acyl fluorides derived from propylene trimer and tetramer failed to undergo this reaction (expts. 15 and 16) as evidenced by substantial absence of methylpropane in the product. This may be attributed to the lower activity of the hydrogen fluoride catalyst and/or the shorter contact time we employed (0.75 *vs.* 2.5 to 4.5 hours).

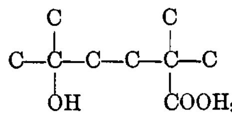
One explanation for the above behavior may be that the electron-withdrawing —COOH or —COF group reduces the reactivity of the tertiary hydrogen and thus effectively retards the hydrogen transfer reaction. This occurs not only in the adjacent alpha position *via* direct inductive effect but also in more distant positions, perhaps *via* quasi ring conformation resulting from bonding of the tertiary hydrogen with carboxyl oxygen.[22]

(22) J. Cason, J. S. Fessenden, and C. L. Agree, *Tetrahedron* 7, 289 (1959).

It may also be postulated that the nonoccurrence of hydrogen transfer is due to the formation of an oxonium ion, $RCOOH_2^+$, which repels the attacking carbonium ion derived from the olefin, alkyl halide, or alcohol.[23] However, the formation of an oxonium ion does not seem to operate to prevent reaction of a distal ethylene bond (as in oleic acid[8,11]) with carbon monoxide. Apparently the protonation of the ethylene bond requires less energy than does the hydride transfer reaction. Similarly the lower energy requirement for the ionization of the hydroxyl group would explain why no difficulty is encountered in converting a ditertiary diol to the corresponding dibasic acid,[24] a reaction which may also involve



a positively charged ion such as (*A*) as an intermediate.



(*A*)

Reactions of aromatic hydrocarbons (*Table III*). In expts. 17 and 18, 2-methylpropene was gradually added to the stirred autoclave containing benzene, carbon monoxide under pressure, and hydrogen fluoride. The ratio of the olefin reacting with carbon monoxide to form pivalic acid (after hydrolysis) to that consumed in the formation of mono- and poly-t-butyl derivatives was 1:3 at 20°. With a more reactive arene such as toluene the ratio was about 1:8 (expt. 19).

No ketone was formed *via*:

$$ArH + t\text{-}C_4H_9COF \xrightarrow{HF} Ar\text{—}CO\text{—}t\text{-}C_4H_9 + HF$$

(23) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **77**, 1803 (1955) offered a similar explanation for the resistance of 1,3,5-ethylxylene to further alkylation.

(24) A. De Benedictis and K. E. Furman, U. S. Patent 2,913,489 (Nov. 17, 1959).

TABLE III

REACTION WITH AROMATICS

Expt. No.	Olefin, Moles	Aromatic, Moles (When added)	Pressure[a]	Time[b]	CO, Moles Absorbed[c]	HF, Moles	Temp.	Products: Acid[d]	Products: Neutrals[e]
17	i-C_4H_8 2	Benzene 6 (initially)	700–535	38	0.86	10.6	20	0.63 mole	t-BuC_6H_5 No ketone
18	i-C_4H_8 2	Benzene 6 (initially)	740–795	28	None	10.3	70	Trace	t-BuC_6H_5 No ketone
19	i-C_4H_8 2	Toluene 7.8 (initially)	650–540	34	0.89	10.3	20	0.24 mole	t-Bu-Tol. No ketone
20	DIB[g] 1.9	Toluene 5 (after olefin)	330	65	0.71	11.1	25[f]	RCOF	Toluene
			375	30			55	RCOF	Toluene
			750	55			80	RCOF	m-R—Tol.
			915	60			100	RCOF	m-R—Tol.
21	None	t-Bu-C_6H_5 2	665–590	7	1.18	10.3	30	Pivalic 0.35 mole	Benzene, tol. &
		Toluene 2		53					t-Bu-Arenes
22	None	Cumene	600–950	121		10.4	95	None	Benzene
				204					p-RC_6H_4R

[a] P.s.i.g. at various stages. [b] Minutes to add and additional stirring in each stage. [c] Estimated by weight increase after run is complete. [d] After hydrolysis. [e] Tol. = toluene; R = alkyl. [f] During olefin/CO reaction and during addition of aromatics. [g] Diisobutylene.

TABLE IV

ACIDS AND DERIVATIVES

Acid	B.P.	Mm.	B.P. (760 Mm.)	n^t	Temp. (t)	M.P.	Amide M.P.
Isobutyric			152–155	1.3930–1.3949	20		
			(153.5–153.8)[b]	(1.3930)[b]	20		
Pivalic	56	6	162–163[a]	1.3859–1.3862	55	34–35	
			(163.7)[n]			35.3–35.5[n]	
1-Methylcyclopentanecarboxylic	102	7.6	218–220[a]	1.4522–1.4528	20		123–124[e]
	(116	16)[c]	(219–219.5)[d]	(1.4529)[c]	20		(124–125)[d]
1-Methylcyclohexanecarboxylic	81	1	233[a]	1.4474–1.4485	55	33.5–34.5[g]	65–66[j,k]
			(233–234)[f]			(39–40)[h]	(65–66)[h]
2,2,3-Trimethylbutanoic[l]	127	40	207[a]	1.4029–1.4031	80	48.5[e]	132–133[j]
	(103	12)[i]	(209)[a,i]			(49.5–50.5)[i]	(131.5–132)[i]
1,4-Dimethylcyclohexanecarboxylic	140	20	240[a]	1.4560–1.4570	20	—	—
(Stereoisomeric)	(136	20)[m]				(35)[m]	(82)[m]
	(143	20)[m]		(1.4606)[m]		—	(134)[m]

[a] Calculated from b.p. at reduced pressure using Group 7 conversions on the Lippencott nomograph, *Ind. Eng. Chem.*, **38,** 320 (1946). [b] J. W. Bruhl, *Ann.*, **200,** 180 (1880). [c] H. Meerwein, *Ann.*, **405,** 171 (1914); **417,** 263 (1918). [d] A. Tschitschibabin, *J. Russ. Phys. Chem. Ges.*, **45,** 186 (1913). [e] From n-heptane. [f] V. N. Ipatieff, J. E. Germain, and H. Pines, *Bull. soc. chim. France*, 259 (1951). [g] From pentane. [h] R. B. Wagner and J. A. Moore, *J. Am. Chem. Soc.*, **72,** 2884 (1950). [i] G. Overberger and M. B. Berenbaum, *J. Am. Chem. Soc.*, **74,** 3293 (1952). [j] From n-hexane. [k] Anilide m.p. 111.5–112°; R. B. Wagner and J. A. Moore, *J. Am. Chem. Soc.*, **72,** 2884 (1950) reported 111.5–112°. [l] Methyl ester 103°/200 mm.; 145°/760 mm.[a], n^{20} 1.4144. [m] Stereoisomers.[5b] [n] A. M. Butlerov, *Ann.*, **173,** 356 (1874).

Even at a higher temperature (70°) there was no acylation of benzene (expt. 18).

It was expected that t-butylarene would be unstable in contact with carbon monoxide and hydrogen fluoride, resulting in conversion to the acyl halide and arene *via* 1a and 2a. This was con-

$$t\text{-}C_4H_9\text{—}Ar + H^+ \underset{b}{\overset{a}{\rightleftharpoons}} t\text{-}C_4H_9^+ + ArH \qquad (1)$$

$$t\text{-}C_4H_9^+ + CO \underset{b}{\overset{a}{\rightleftharpoons}} t\text{-}C_4H_9\overset{+}{C}O \qquad (2)$$

firmed in expt. 21 where t-butylbenzene formed about 17% of pivalic acid at 30°. Thus the results of the "competition" reactions of 2-methylpropene with carbon monoxide and arene must be interpreted in the light of the equilibrium reactions 1 and 2.

Cumene does not undergo reactions of the type 1a and 2a even at 95°; no isobutyric acid was produced on reaction with carbon monoxide (expt. 22), although some disproportionation to benzene and disubstituted benzenes occurred.

In expt. 20 toluene was added to the acyl fluoride product formed from diisobutylene, excess carbon monoxide, and hydrogen fluoride and the contents sampled as the temperature was raised stepwise. At 25° and 55° the only products were acyl fluoride and toluene; and at 80° and 100°, acyl fluoride and m-alkylated toluene. This showed that the reaction sequence 2b and 1b leading to alkylation does not tend to take place with toluene at temperatures below 55°. No ketone was observed in any of the products.

EXPERIMENTAL

Materials. The anhydrous hydrogen fluoride and carbon monoxide were obtained from the Matheson Co. and the pure grade paraffins and cycloparaffins, except decalin and 1,4-dimethylcyclohexane, from Phillips. Eastman decalin was washed with 96% sulfuric acid, water, and alkali; fractionation yielded 99% pure *cis*- and *trans*-decalin. Hydrogenation of *p*-xylene (99%) over a platinum-alumina catalyst afforded a 30:70 mixture of *cis*- and *trans*-1,4-dimethylcyclohexane.

Condensation reaction. The requisite amount of hydrogen fluoride was charged into the evacuated 2-l. stainless steel Magne-dash[25] autoclave. Carbon monoxide was then pressured into the autoclave, a bath placed around the autoclave, and the stirring was started. The olefin feed was slowly pressured into the stirred autoclave from a blowcase. Stirring was continued for a short period, after which the contents of the autoclave were discharged into a train consisting of a polyethylene bottle containing a weighed amount of ice and water, a water scrubber, drier, cold (−80°) trap, and a wet testmeter. Carbon monoxide absorption was measured by weight gain. When a solvent was employed in the condensation, it was added from a blowcase or pressure vessel usually prior to addition of carbon monoxide. The contents in the polyethylene bottle was stabilized by warming to 30°. The organic layer was separated, washed with ice water, and stabilized at about 60° to recover additional condensible gases, *e.g.* propane or 2-methylpropane.

The aqueous and wash layers were combined, saturated with sodium sulfate, and extracted with pentane to recover water-soluble organic acids. The pentane extract and organic layer were combined and stirred with warm alkali until the acyl fluorides were completely hydrolyzed (disappearance of infrared band at approximately 5.5 μ). The alkali-insoluble layer, if any, was separated and the soap solution extracted with pentane to remove traces of neutral oil. Acidification of the soap solution with hydrochloric acid yielded a layer of organic acids. The acidulated aqueous layer was saturated with sodium sulfate and extracted several times with pentane to recover water-soluble organic acids. Distillation afforded the acids described in Table IV.

Identification of products. In general the products were characterized by comparing boiling points, melting points, refractive indices, infrared and mass spectra (for hydrocarbons), and gas liquid chromatograms with that of known standards.

(25) Autoclave Engineers, Inc., Erie, Pa.

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[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE UNIVERSITY]

Effects of Temperature and Catalyst Variation upon the Stereochemistry of Hydrogenation of Disubstituted Benzenes[1]

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The hydrogenation of the three xylenes on platinum oxide gave appreciable yields of *trans*-dimethylcyclohexanes in the order *para* > *meta* > *ortho*. The yield of *trans* isomers increased with temperature, but did not appear to be greatly affected by pressure changes within the pressure ranges used. The yields of the *trans* isomers from the hydrogenation of the xylenes on Raney nickel were in the order *meta* > *ortho* > *para*. Hydrogenation of diethyl phthalate on nickel gave significant amounts of the *trans* product, in contrast to hydrogenation on platinum oxide. Attempts to isomerize *cis*-disubstituted cyclohexanes on either catalyst did not give sufficient amounts of the *trans* isomers to account for the *trans* products of hydrogenation. It is concluded that the *trans* products must be formed during the hydrogenation process, and that the stereochemical course of this process is determined mainly by the nature and positions of the substituents and by the catalyst.

Early studies of the stereochemistry of the catalytic hydrogenation of aromatic compounds led to the formulation of the von Auwers-Skita rules[2,3] which states that *cis* isomers are produced by hydrogenation on platinum in acidic media and *trans* isomers are produced by hydrogenation on platinum in basic media or on nickel in the vapor phase. These generalizations do not allow for the possibility of isomerization process.

Horiuti and Polanyi[4] have proposed that the mechanism of catalytic hydrogenation involves dissociation and chemisorption of hydrogen on the catalyst surface and chemisorption of the substrate, followed by addition of hydrogen to the substrate one atom at a time, the addition of each atom of hydrogen being accompanied by desorption at the point to which the hydrogen was added. All steps are reversible.

The hydrogenation of a large number of polynuclear aromatic compounds on Adams' platinum oxide catalyst in glacial acetic acid at room temperature gave stereochemical results which suggested to Linstead and his co-workers[5] that a single aromatic ring must be hydrogenated in a single period of adsorption, with all of the hydrogen being added from the same side of the ring to produce a *cis* product. Such a process requires that the aromatic ring be adsorbed parallel to the catalyst surface. Some kinetic studies,[6] however, have made it necessary to consider the possibility, in mononuclear systems at least, of other orientations of the adsorbed ring.

(1) Taken in part from the Doctoral dissertation of L. R. Caswell, Michigan State University, 1956.

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(3) K. von Auwers, *Ann.*, **420**, 84 (1925).

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(6) H. A. Smith and H. T. Meriwether, *J. Am. Chem. Soc.*, **71**, 413 (1949).