was 116.5; the calculated value for 1-phenyl-1,3-*cis*-cyclopentanedicarboxylic acid is 117.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.47; H, 5.99.

1-Phenylnorbornane (XXV. R = C_6H_5). The Huang-Minlon modification[55] of Wolff-Kishner reduction was employed. The quantities of materials used were 14.9 g. (0.08 mole) of 1-phenyl-2-norbornanone (XIV. Ar = C_6H_5), 10 g. of potassium hydroxide, 75 ml. of ethylene glycol and 9 ml. of hydrazine hydrate. The combined distillate and cooled reflux mixture were poured into water, extracted with ligroin and the combined extracts were dried with anhydrous sodium sulfate. After the ligroin was removed at reduced pressure, the residue was distilled to give 12.2 g. (88.3% yield) of very light yellow oil, b.p. 124–128° (16 mm.), n_D^{20} 1.5437.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.91; H, 9.34.

The NMR spectrum showed absorptions, in τ units, at 2.849 for the five phenyl hydrogens, at 7.68 for the C-4 bridgehead hydrogen and at 8.383 (shoulder at 8.63) for the remaining ten hydrogens.

1-p-Anisylnorbornane (XXV, R = p-$CH_3OC_6H_4$). The similar reduction of 3.0 g. (0.014 mole) of 1-*p*-anisyl-2-norbornanone (XIV, Ar = p-$CH_3OC_6H_4$) gave 1.8 g. (63.6% yield) of 1-*p*-anisylnorbornane (XXV, R = p-$CH_3OC_6H_4$), b.p. 128–132°. This was oxidized directly (see below).

Norbornane-1-carboxylic acid (XXV, R = COOH). Ozonization of 1.8 g. of 1-*p*-anisylnorbornane (XXV, R = p-$CH_3OC_6H_4$) was carried out in 75 ml. of dichloromethane as described by Bartlett, Webster, Dills, and Richey[6] for the oxidation of *p*-anisylapocyclene to tricyclenic acid. The basic solution obtained during the work-up was extracted with ether to remove neutral material and then acidified with dilute hydrochloric acid. After heavily salting the solution, it was extracted with ether several times. The combined ether extracts were dried over sodium sulfate, the ether evaporated leaving a yellow oil. Sublimation afforded 240 mg. (19.0% yield) of white crystals, m.p. 111.4–112.3°, after three recrystallizations from ligroin (lit. m.p. 111–112,[49d] 112–113,[49c] and 113.8–115.5°[49b]). A direct comparison with an authentic sample of norbornane-1-carboxylic acid proved the identity.[49]

Acknowledgment. Partial support of this research by a grant from the National Science Foundation is acknowledged with appreciation. We are indebted to Dr. George Van Dyke Tiers, Minnesota Mining and Manufacturing Co., for the determination and interpretation of the NMR spectra.

PRINCETON, N. J.

---

[55] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946); **70**, 2802 (1948); **71**, 3301 (1949).

[CONTRIBUTION FROM THE SINCLAIR RESEARCH LABORATORIES]

Ester Formation in the Hydrogen Fluoride-Catalyzed Reaction of Olefins with Carbon Monoxide

B. S. FRIEDMAN AND S. M. COTTON

Received April 14, 1961

Esters are produced in fair yield along with acyl fluorides and organic acids by condensation of unbranched olefins with carbon monoxide in the presence of hydrogen fluoride containing small amounts of water. Branched olefins yield only acyl fluorides and acids. Possible mechanisms for the ester formation are discussed.

H. Koch has shown that olefins react rapidly with carbon monoxide at room temperature and moderate pressures in the presence of catalysts such as concentrated sulfuric acid.[1a,1b] anhydrous hydrogen fluoride,[1c] monohydroxyfluoboric acid,[1d] and mixtures of the latter with phosphoric or sulfuric acid.[1d] These reactions are the basis of an elegant synthesis of branched organic acids which are formed by hydrolyzing the reactions products with water. He postulated[1e] the following mechanism:

$$\text{Olefin} + H^+ \longrightarrow R^+$$

$$R^+ + CO \longrightarrow RCO^+$$

$$RCO^+ + HOH \longrightarrow RCOOH + H^+$$

We have confirmed Koch's indication that anhydrous hydrogen fluoride is a powerful catalyst for the olefin–carbon monoxide reaction. However, since the hydrogen fluoride recovered for recycle from the final water–organic acid–catalyst mixture is apt to contain water, the use of "wet" hydrogen fluoride as catalyst[2] was investigated. Our study showed that relatively minor amounts of water in the catalyst affect the course of the reaction and the nature of the products obtained from various types of olefins.

Unbranched olefins (Table I). The reaction of propylene with carbon monoxide in the presence of anhydrous hydrogen fluoride at room temperature resulted in low yields of acyl fluoride and considerable isopropyl fluoride. At a higher temperature, namely 75° (Experiment 1), more acyl fluoride was produced (isolated as acid after hydrolysis) and a slightly smaller amount of isopropyl fluoride. An attempt was made (Experiment 2) to improve the yield of acid from propylene and lessen the amount of isopropyl fluoride by using a catalyst containing water (19.8%). With this catalyst carbon monoxide absorption was negligible until the temperature was

---

[1] (a) H. Koch, *Brennstoff Chem.*, **36**, 321 (1955). (b) *Riv dei Combustibili*, **10**, 77 (1956). (c) U. S. Patent 2,831,877 (April 22, 1958). (d) U. S. Patent **2,876,241** (March 3, (1959). (e) *Fette und Seifen*, **59**, 493 (1957).

[2] B. S. Friedman and S. M. Cotton, U. S. Patent **2,975,199** (March 14, 1961).

TABLE I

UNBRANCHED OLEFINS

Expt. No.	Olefin, Moles	Carbon Monoxide		Hydrogen Fluoride, Moles	Water, Moles, Wt. %[d]	Temp., Time[e]	Products[f]	Wt., G.	Moles	Yield[g]
		Pressure,[a] Moles[b]	Molar Ratio[c]							
1	Propylene	550–305	0.48	10.2	None	75	Isobutyric acid	46	0.52	14
	3.67	1.75					Heavier acids	135	—	—
							Isopropyl fluoride	50[j]	0.81	22
							Isohexenes	11[i]	0.13	7
							Alkali-insolubles[h]	83		
2	Propylene	585–350	0.43	10.5	2.9[i]	100	Isobutyric and heavier			
	3.88	1.68			19.8	67/300	acids	200		
							Esters	35		
3	Butene-1	580–410	0.42	12.2	None	30	*s*-Butyl fluoride	31[j]	0.41	12
	3.54	1.43				39/30	Olefin liquid	4[j]		
							Acids	201		
4	Butene-1	540–385	0.48	10.5	0.61[i]	30	2-Methylbutyric acid	70	0.67	22
	2.95	1.45			5	90/70	C_9 acids	32	0.19	13
							Heavier acids	26		
							s-Butyl 2-methylbutanoate[k]	48	0.31	21
							s-Butyl isononates[l]	22	0.11	11
5	Butene-1	430–290	0.46	12.3	1.55[i]	60	Acids	166		
	3.01	1.39			10.2	39/37	*s*-Butyl 2-methylbutanate	13		
							Higher esters	14		
6	Butene-1	635–320	0.57	13	6.1[i]	100	Entire product is acid			
	3.54	2			29.9	90/185				
7	Butene-1	550–435	0.4	13.2	0.44[i]	30	Acids	93		
	2.84	1.14			1.39[m]	34/31	*s*-Butyl 2-methylbutanoate	80	0.51	36
					3[n]		Higher esters	10		
8	Butene-1	425–370	0.32	10.8	0.61[i]	30	Acids		0.26	
	2.97	0.95			1.61[m]	120/50	*s*-Butyl 2-methylbutanoate	102	0.65	44
					5[n]		*s*-Butylisononates	72	0.34	34
9	Cyclo-hexene	500–450	0.38	12.1	0.67[i]	30	1-MCP acid[o]	18	0.14	5
	3	1.14			1.67[m]	55/90	CH acid[p]	79	0.62	21
					5[n]		Higher acids	67		
							Esters[q]	106	0.51	34
10	Octene-1	490–365	0.57	10.6	0.61[i]	30	Acids		1.15	
	2.9	1.64			1.94[m]	100/10	*s*-Octylisononates[r]	123	0.46	32
					5[n]		Higher esters	27		

[a] Range, p.s.i.g. [b] Absorbed, estimated from weight increase of liquid product. [c] Moles carbon monoxide absorbed per mole olefin. [d] Concentration of water in catalyst. [e] Minutes to add/minutes further stirring. [f] After hydrolysis. [g] Wt. % based on olefin feed. [h] About 50–50 ester and alcohol. [i] Initially present. [j] Condensed in Dry Ice trap. [k] B.p. 168°, n^{20}_{D} 1.4039–1.4043; P. A. Guye and J. Guerchgorine, *Compt. rend.*, **124**, 232 (1897) reported b.p. 164–167°. [l] B.p. 247–250; n^{20}_{D} 1.4300–1.4307. [m] Total. [n] Maintained during addition of olefin. [o] Methylcyclopentanecarboxylic acid. [p] Cyclohexanecarboxylic acid. [q] Contains 0.27 mole (18% yield) of cyclohexyl cyclohexanecarboxylate, b.p. 268–271°, n^{20}_{D} 1.4725; lit.: 132°/10 mm. = 268° (Fr. Ficter and W. Siegrist, *Helv. Chim. Acta*, **15**, 698 (1932). [r] B.p. 275–302°, n^{20}_{D} 1.4333–1.4342. Calcd. for $C_{17}H_{34}O_2$: C, 75.5; H, 12.67. Found: C, 75.42; H, 12.67.

raised to about 100°. Practically no isopropyl fluoride was produced, the propylene feed being converted in good yield to a mixture of isobutyric and heavier acids.

Butene-1 was much more reactive than propylene, and reacted readily at room temperature in the presence of anhydrous or 95% hydrogen fluoride. Anhydrous hydrogen fluoride afforded considerable organic acids plus 12% *sec*-butyl fluoride (Experiment 3). However, the product obtained with the 95% catalyst (Experiment 4) contained esters as well as acids (2-methylbutyric, and C_9 heavier). The esters consisted of *sec*-butyl 2-methylbutanoate (21% yield) and *sec*-butyl isononates (11%).

Apparently when the catalyst contains water, the carbonium ion derived from the incoming olefin can react either with carbon monoxide or water as follows:

$$R^+ + CO \rightleftharpoons RCO^+ \quad (1)$$

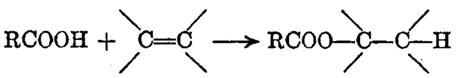
$$R^+ + HOH \rightleftharpoons ROH + H^+ \quad (2)$$

The resulting products can then interact to form an ester:

$$RCO^+ + ROH \rightleftharpoons RCOOR + H^+ \quad (3)$$

However, it is also possible that esters are formed *via in situ* hydrolysis of acyl fluoride to organic acid followed by reaction of the latter with incoming olefin:

$$RCOF + HOH \longrightarrow RCOOH + HF \quad (4)$$



$$RCOOH + \mathrm{>C{=}C<} \longrightarrow RCOO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \quad (5)$$

The latter mechanism (Equations 4 and 5) was given support by the results obtained in treating

TABLE II

BRANCHED OLEFINS

Expt. No.	Olefin[a] Moles	Carbon Monoxide		Hydrogen Fluoride		Temp., Time[e]	Yield[f] of Acids				Total	Hydrolysis Wt. %[h]
		Pressure,[b] Moles[c]	Molar Ratio[d]	Moles	Concn.		C-5	C-9[g]	C-13[g]	C-17[g]		
11	DIB 3.66	800–405 4.88	0.75	8	Anhyd.	15 90/10	10	35	24	7	76	<1
12	DIB 6.33	500–70 5.08	0.8	14	90	20 143/10	16	37	11	13	77	37
13	DIB 5.85	500–150 5.33	0.91	12.2	80	40 148/25	9	46	31	10	96	70
14	DIB 5.93	500–190 4.3	0.73	11.1	75	60 166/54	9	47	9	13	78	92
15	DIB 3.7	450–215 0.64	0.17	10.2	67	90 165/22		(Not distilled)				
16	PrT 2.9	485–320 3.57	1.23	10.8	95	30 77/49			86		[i]	

[a] DIB = diisobutylene; PrT = propylene tetramer. [b] Range, p.s.i.g. [c] Absorbed, estimated from weight increase of liquid products. [d] Moles carbon monoxide absorbed per mole olefin. [e] Minutes to add/minutes further stirring. [f] Wt. % theoretical based on olefin feed. [g] Average mol. wt. [h] Conversion of RCOF to RCOOH during reaction of olefin with carbon monoxide. [i] 51 g. <C_{13} acids, b.p. 173–247°, 536 g. C_{13}, 247–298°, 74 g. >C_{13}.

hexene-1 with acetic acid in the presence of anhydrous hydrogen fluoride at room temperature (no carbon monoxide present). Hexylacetates were formed in 33% yield. Similar results have been reported by others.[3]

Since the water initially present is soon consumed in forming organic acid and/or ester, it was of interest to evaluate the effect of maintaining the water content of the catalyst by injecting water concomitantly with the olefin. This was done in Experiment 8 where water was injected continuously to maintain catalyst water at 5%. The over-all result was a very considerable increase in yield of esters (44% *sec*-butyl 2-methylbutanoate and 34% *sec*-butyl isononates) over that obtained when all the water was added initially as in Experiment 5. In the latter test the resulting catalyst mixture was relatively inactive at room temperature and reasonably rapid absorption of carbon monoxide occurred only when the temperature was raised to 60°. If still more water is added initially, *e.g.*, 29.9% (Experiment 6), the catalyst is so weakened that a much higher temperature (100°) must be employed to effect carbon monoxide absorption. The product obtained under these conditions contained only organic acids—no acyl fluoride or ester was present.

A lower rate of water injection (3% *vs.* 5%) resulted in a lower yield of ester (Experiment 7 *vs.* 8).

Octene-1 in the presence of hydrogen fluoride diluted continuously with 5% water (Experiment 10) produced acids and a large amount of ester consisting mainly of secondary octyl esters of C_9 acids. In a similar operation (Experiment 9) cyclohexene yielded 5% of 1-methylcyclopentanecarboxylic acid, 21% of cyclohexane-carboxylic acid, and 34% of the cyclohexyl esters of these acids.

Koch has reported[1b] obtaining a mixture of alcohol, ester, and organic acid on treating propylene with carbon monoxide in the presence of concentrated sulfuric acid. He gave no experimental or analytical data but indicated that the proportions of these products could be varied according to the conditions, *e.g.*, mole ratio of olefin to sulfuric acid. In a recent paper[4] he and his co-worker mentioned the isolation of *sec*-butyl 2-methylbutyrate as a by-product of the acid synthesis involving treatment of *n*-butene with carbon monoxide in the presence of boron fluoride-dihydrate catalyst. No yields were given.

Branched olefins (Table II). Diisobutylene reacted readily with carbon monoxide in the presence of hydrogen fluoride containing a small amount of water, to give excellent yields of acids, but little or no esters. As reported by Koch for results obtained with sulfuric acid, the acid-catalyzed cleavage, polymerization, and disproportionation of the diisobutylene prior to condensation with carbon monoxide led to the formation of considerable amounts of by-product C_5 (pivalic), C_{13} and C_{17} acids. The optimum yield of intact (C_9) acid and of C_{13} acid was obtained with the 80% catalyst (Experiment 13).

It has been shown in arene alkylation studies,[5] that propylene polymers such as the tetramer are much less susceptible than isobutylene polymers to cleavage and disproportionation reactions. A similar behavior was noted in condensation of the tetramer with carbon monoxide (Experiment 16); the yield of intact (C_{13}) acid was 86%.

Absorption of carbon monoxide was rapid at 15 to 20° either with the anhydrous or 90% catalyst. However, in order to maintain a reasonably rapid carbon monoxide absorption rate, it was necessary

---

(3) R. D. Morin and A. E. Bearse, *Ind. Eng. Chem.*, **43**, 1596 (1951) obtained 55% of isopropyl acetate on treating propylene with acetic acid at 100° in the presence of hydrogen fluoride.

(4) H. Koch and W. Haaf, *Ann.*, **638**, 111 (1960).

(5)(a) R. J. Lee, H. M. Knight and J. T. Kelly, *Ind. Eng. Chem.*, **50**, 1001 (1958); (b) N. V. de Bataafsche Petroleum Maatschappij, Brit. Patent **706,653** (March 31, 1954).

to increase the temperature to 40° for the 80% catalyst and to 60° for the 75% catalyst. Absorption was very slow and incomplete with the 67% catalyst—even at 90°.

As expected, the initially-formed acyl fluorides were increasingly hydrolyzed to the corresponding acids as the water content of the catalyst was increased and the temperature raised (as required for rapid carbon monoxide absorption).

The substantial absence of esters in the reaction of branched olefins with carbon monoxide and diluted hydrogen fluoride may be attributed (a) to the instability, in the presence of concentrated hydrogen fluoride and carbon monoxide, of the intermediate tertiary alcohol (reversing Equation 2), and (b) to the instability of any *t*-alkyl ester that may have formed (reversing Equation 3).

Mixed olefin feed. Since branched olefins react more readily with carbon monoxide in the presence of diluted hydrogen fluoride than do straight-chain olefins, it was thought that operation with a mixture of each type of olefin would result in the formation of *sec*-alkyl esters of tertiary acids. Thus the isoolefin should react much more rapidly than the unbranched olefin with carbon monoxide forming *t*-acyl fluoride which would be converted to *t*-acid by the water in the catalyst, and the *t*-acid would in turn react with the incoming unbranched olefin to yield a secondary alkyl ester of the tertiary acid.

This general idea was tested by injecting a mixture of 2-methylpropene and butene-1 into a stirred autoclave containing carbon monoxide and 90.7% hydrogen fluoride at 25°. The product contained 77 g. of ester and 169 g. of organic acid. However, only 7% of the expected *sec*-butyl pivalate was present.

A similar test made with a mixture of 2-methylpropene and propene using hydrogen fluoride diluted continuously with 4% water yielded mostly acids. A small amount of esters was formed, the yield of the expected isopropyl pivalate amounting to only 6%.

EXPERIMENTAL

Materials. The gases employed were Matheson anhydrous hydrogen fluoride (99.9%) and commercial grade carbon monoxide (98%), and Phillips butene-1 (99%), propylene (99%), and isobutylene (99%). The diisobutylene was Eastman "practical" grade; the octene-1 and cyclohexene were Phillips 99% grade; the propylene tetramer was a heart cut (b.p. range 180–198°) of the commercial polymer.

General procedure. A Magnedash autoclave equipped with a 2-l. Hastalloy "C" pot was employed for most of the tests. The balance were conducted in a 2-l. stainless steel stirred autoclave. The hydrogen fluoride catalyst was pressured into the autoclave after which carbon monoxide was injected with stirring to the desired pressure. The olefin was then charged gradually at a rate that permitted control of the temperature of the autoclave contents. Carbon monoxide was injected as required to maintain pressure. Stirring was then continued for an additional period.

In Experiments 11 to 15 the contents of the autoclave was discharged into a polyethylene bottle cooled with Dry Ice. A portion of this was added dropwise with stirring to excess concentrated ammonium hydroxide at −20 to −25° and stirred with warming to room temperature. Concentrated hydrogen chloride was added to *p*H 2 and the solution extracted with pentane. The pentane solution was washed with saturated sodium sulfate solution to remove traces of hydrogen chloride or ammonium chloride. Titration of the pentane solution with alkali gave the amount of organic acids present in the autoclave effluent, and determination of bound nitrogen present (amides) by Kjeldahl gave the amount of acyl fluoride.

The balance of the autoclave liquid effluent was poured with stirring onto precooled (−80°) crushed ice, warmed to room temperature, and worked up as below.

In the remaining experiments the autoclave contents were discharged into crushed ice and the organic layer washed with aqueous sodium sulfate. The aqueous layers were combined and extracted with pentane. The organic layer and pentane washes were combined and neutralized with potassium hydroxide solution. Some heating was required to convert all the acyl fluoride to soaps, as evidenced by disappearance of the infrared absorption band in the region 5.4 to 5.5μ. The insoluble layer (neutrals) was separated, and the soap was extracted with pentane for more complete removal of neutral by-products and then acidified to liberate the organic acids. After removal of the organic acid layer, the acidified aqueous layer was extracted with pentane for better recovery of the water soluble organic acids. Vacuum distillation afforded fractions of various molecular weights.

Identification of products. In general the products were characterized by comparing boiling points, refractive indices, infrared spectra, and gas liquid chromatograms with that of known standards. Cyclohexyl esters of cyclohexanecarboxylic acids and methylcyclopentanecarboxylic acids were prepared by treatment of the acids with thionyl chloride followed by boiling with cyclohexyl alcohol and a trace of pyridine; *sec*-butyl 2-methylbutyrate by treating 2-methylbutyryl chloride with *sec*-butanol; isopropyl pivalate by treating pivalyl fluoride with isopropyl alcohol. 2-Methylbutyric acid was purchased from Eastman.

The *sec*-butylisononate product was characterized by stirring and heating 10 g. with 10 ml. dipropylene glycol and 6 g. of potassium hydroxide at 160° for 0.5 hr. The liquid which distilled over during the saponification was identified as *sec*-butyl alcohol, 98.3% pure; yield 80%.

HARVEY, ILL.