# Organic Reactions in Liquid Hydrogen Fluoride. III.[1] Carboxylic Acids from Olefins and Carbon Monoxide (Hydrogen Fluoride–Koch Reaction)

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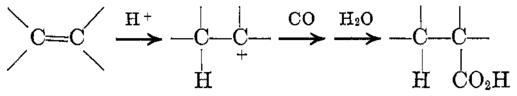
Linear and cyclic olefins are converted to carboxylic acids in 85–95% aqueous hydrogen fluoride under a pressure of 1000–2500 psig of carbon monoxide at 20–50°. 1-Pentene yields a mixture of the "iso" acids, α-ethylbutyric and α-methylvaleric acids, and the "neo" acid, α,α-dimethylbutyric acid. When the reaction product of cyclohexene, HF, and CO is hydrolyzed with water, the chief products are cyclohexanecarboxylic and 1-methylcyclopentanecarboxylic acids. If methanol is added to the reaction, the novel 2-(cyclohexenyl)cyclohexyl cyclohexyl ketone is isolated, in addition to the expected methyl esters of the above acids. Linear long-chain internal olefins, such as 7-tetradecene, give carboxylic acid yields of 65–80%. 2-Methylbutene gives a 57% yield of α,α-dimethylbutyric acid; with cyclododecene, a low yield of the expected 12-membered ring acid admixed with transannular products is obtained. The diolefin 1,5-cyclooctadiene gives the ring-contracted acid bicyclo[3.3.0]octane-2-carboxylic acid in low yield.

As a continuance of our studies on reactions in liquid hydrogen fluoride, we examined the condensation of carbon monoxide with various olefins to produce carboxylic acids. Termed the Koch reaction,[2] carboxylic acids are produced by contacting an olefin, alcohol, or halide with moderate to high pressures (500–2000 psig) of carbon monoxide in the presence of solvent quantities of an acid catalyst, usually sulfuric. Dilution with water liberates the carboxylic acid. Cursory examinations of the Koch reaction using a hydrogen fluoride catalyst solvent system have been reported[3] by various workers, the most extensive work having been done by Takezaki, *et al.* The kinetics of the reaction of propylene with carbon monoxide in HF–$H_2O$ to form isoisobutyric acid was studied.

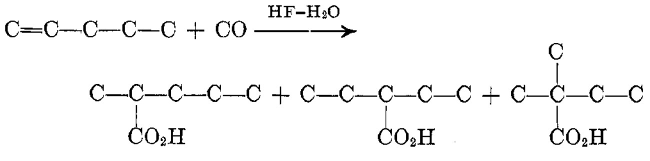


$$>C{=}C< \xrightarrow{H^+} -\underset{H}{\overset{|}{C}}-\underset{+}{\overset{|}{C}}- \xrightarrow{CO} \xrightarrow{H_2O} -\underset{H}{\overset{|}{C}}-\underset{CO_2H}{\overset{|}{C}}-$$

This report describes the reaction of carbon monoxide with pentene, as a typical linear olefin, and with cyclohexene, as a typical cyclic olefin. Reactions with a few miscellaneous olefins in liquid hydrogen fluoride are also discussed.

**HF–Koch Reaction with 1-Pentene.**—1-Pentene was employed to investigate various fundamental parameters of the reaction chiefly because only three carboxylic acids are likely: 2-methylvaleric (**1**), 2-ethylbutyric (**2**), and 2,2-dimethylbutyric acid, the "neo" acid (**3**). Current protonation and carbonium ion theories exclude a fourth isomer, *n*-hexanoic acid.

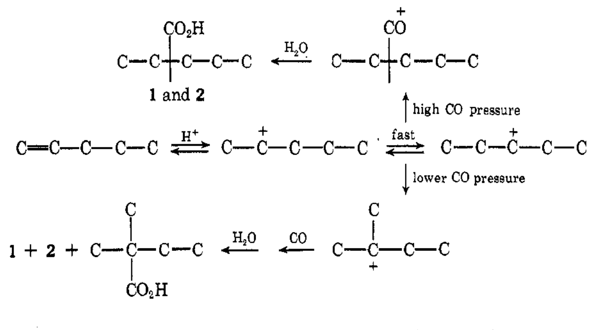
The reaction is carried out by placing HF in a Monel reactor, pressuring the system with the desired amount of carbon monoxide, and then pumping the olefin into the reactor. This method tends to minimize the amount of self-esters and neutral oligomers formed as described by Friedman and Cotton.[3a,b] The significant variable is the molar ratio of HF to pentene (see Table I). Pressure, amount of water present, time, and temperature affect isolated yields of $C_6$ carboxylic acids to a lesser extent.



$$C{=}C{-}C{-}C{-}C + CO \xrightarrow{HF-H_2O} C{-}\underset{CO_2H}{C}{-}C{-}C{-}C + C{-}C{-}\underset{CO_2H}{C}{-}C{-}C + C{-}\overset{C}{\underset{CO_2H}{C}}{-}C{-}C$$

**1** **2** **3**

**Pressure Effects.**—Aside from yield data, the variances in pressure can have a pronounced effect on the isomerization of the carbon chain. For example, in comparable runs (runs 1 and 3) the selectivity toward neo acid formation, **3**, decreases from 38 to 14%, as the pressure is increased. This indicates that at higher pressures carbon monoxide tends to intercept the secondary carbonium ion prior to skeletal rearrangement to the tertiary, thus forming enhanced amounts of the "iso" acids.



At lower pressures, thermodynamic equilibrium of the carbonium ions tends to be favored and larger quantities of the "neo" acid are obtained resulting from increased isomerization. More importantly, the higher the ratio of HF to olefin, the greater the total yield of carboxylic acids.

**Temperature Effects.**—The ideal range for practical carboxylation appears to be 10–50°. Above 50°, polymerization[4] of the olefin becomes predominant and below 10° the reaction is too slow.

**Isomerization Studies.**—The relative amounts of "neo" and "iso" acids depend both on pressure and amount of contact with the acid phase. Eidus,[5] in a

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[1] For paper II, see J. R. Norell, *J. Org. Chem.*, **35**, 1619 (1970).

[2] For a recent review see J. Falbe, "Carbon Monoxide in Organic Synthesis," Springer-Verlag, New York, N. Y., 1970, p 123 ff.

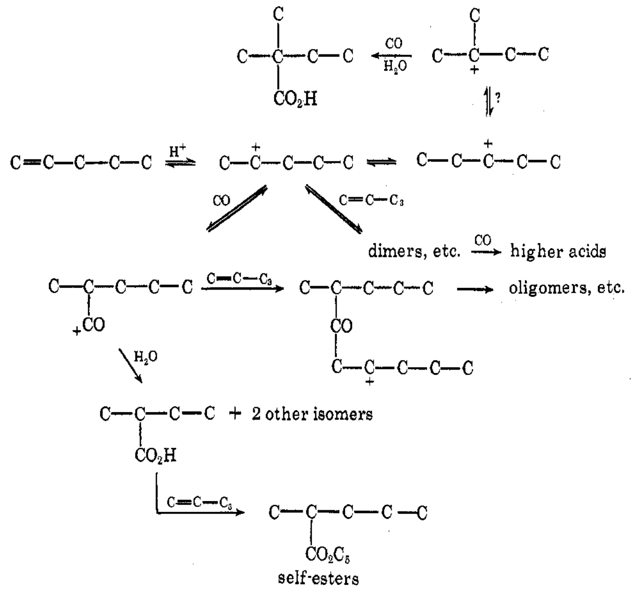
[3] (a) B. S. Friedman and S. M. Cotton, *J. Org. Chem.*, **26**, 3751 (1961); (b) *ibid.*, **27**, 481 (1962); (c) Armour and Co., French Patent 1,477,330 (Mar 6, 1967); (d) Y. Takezaki, Y. Fuchigami, H. Ternaishi, N. Sugita, and K. Kudo, *Bull. Jap. Petrol. Inst.*, **8**, 31 (1966); (e) Shell-Internationale Research Maatschappij, N. Y., British Patent 1,167,116 (Oct 15, 1969).

[4] G. A. Olah and Y. Halpern, *J. Org. Chem.* **36**, 2354 (1971).

[5] Y. T. Eidus, K. V. Puzitskii, and O. D. Sterligov, *Zh. Obshch. Khim.*, **30**, 3799 (1960).

carbomethoxylation study on 1-pentene in sulfuric acid and methanol with carbon monoxide, reports only the esters of acids **2** and **3**; no mention is made of the 2 isomer. In contrast, we have found that all three of the possible isomers are present in substantial amounts. The ratio of "neo" to "iso" acid was obtained by glc; however, α-ethylbutyric and α-methylvaleric acids or their methyl esters could not be separated on a 150-ft capillary column. Use of mass spectrometry permitted the quantitative determination of all three acids simultaneously with a ±5% error. Acids **1** and **2** rearrange in the mass spectrometer *via* a McLafferty rearrangement with the former providing propylene and a mass peak of 74 and the latter ethylene and a fragment of 88. Acid **3** cleaves, giving a $C_5H_{12}^+$ of 71 and a $\cdot CO_2H$ fragment. By determining the sensitivity coefficients for pure acids and employing three equations and three unknowns, one can calculate the amount of each acid present based on the above fragmentations. As shown in Table I, both the 2 and 3 isomers were obtained, with substitution at the third carbon prevailing slightly.

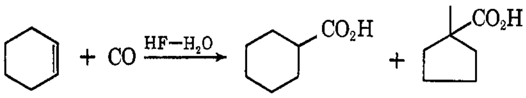
Examination of the over-all picture of the CO carboxylation of 1-pentene indicates a variety of paths.



The above scheme shows that, for optimization of yield, CO pressure should be increased, temperature decreased, and olefin added very slowly to the reaction mixture so as to avoid an excess of olefin. Water is necessary in the system to facilitate hydrolysis of the intermediate acyl fluoride and to prevent extensive oligomerization. The need for a high HF to olefin ratio is not immediately recognized, but the larger amount of HF probably provides a more desirable solvent effect for both the CO and hydrocarbon and gives a higher degree of initial protonation (as was observed in our earlier work on the reaction of olefins and nitriles).[1]

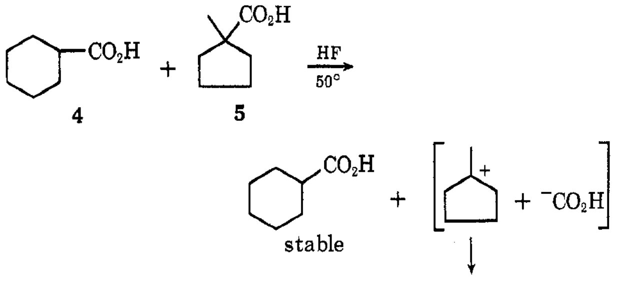
**Cyclohexene.**—Using cyclohexene as a typical cyclic olefin, its carboxylation was investigated. Earlier, by treating cyclohexene with CO (700 psig) in $H_2SO_4$, Koch[6] had obtained a 28% yield of a 3:2 mixture of cyclohexanecarboxylic acid (**4**) and 1-methylcyclopentanecarboxylic acid (**5**). Using methanol to quench the reaction mixture, Eidus, *et al.*,[7] obtained a 50% yield of the methyl esters with 1100 psig CO in sulfuric acid the ratio of the cyclohexane to cyclopentanecarboxylic acids being 4:5. Friedman and Cotton[3a] reported a 26% yield of cyclic $C_6$ acids with CO (500 psig), HF, and water followed by quenching with methanol. In this case the ratio of **4** to **5** was 4:1.

Employing higher CO pressures and an 8:1 ratio of HF to $H_2O$, we were able to obtain 84% distilled yields of the cyclic acids. The increase in pressure permits CO attack prior to ring contraction.



| | 4 | 5 | Yield % |
|---|---|---|---|
| 1000 psig | 73 | 27 | 84 |
| 2500 psig | 89 | 11 | 73 |

If, during the work-up procedure, attempts are made to distil the HF out of the reactor prior to addition of water, the yield of distilled acid is reduced to 30%; however, the isomer ratio becomes 92.5% **4** and 7.5% **5**. The observation is rationalized by assuming that initially similar yields are produced in all cases, but as the fluoride reaction mixture is concentrated by heating at 50° and pulling a water pump vacuum, the tertiary acid **5** decarboxylates and polymerizes or self-esterifies. The cyclohexyl acid, being a secondary acid, is more stable under these conditions and does not degrade. Both **4** and **5** will readily decompose at 100° in HF, but **4** is relatively stable in HF at 50°. Thus, the over-all effect of heating the acid mixture is a decrease in isolated yield, an increase in neutrals, and an increase in percentage of the cyclohexyl acid present.



A new reaction producing a novel ketone occurred when cyclohexene was treated with carbon monoxide in the presence of hydrogen fluoride followed by addition of methanol in place of water. In addition to 37% yield of the methyl esters of cyclohexanecarboxylic acid and 1-methylcyclopentanecarboxylic acid in a 91:9 ratio, there was obtained a 23% yield of the novel ketone, 2-(cyclohexenyl)cyclohexyl cyclohexyl ketone (**6**).

The compound was characterized by noting that the infrared spectrum contained a strong carbonyl band at 5.9 μ. No OH bands at 3.0 μ were found. The nmr spectrum indicated a ketone (τ 7.8) rather than an aldehyde. A broad absorption between τ 7.5 and 9.2 is produced by cyclic methylene groups which shield the protons adjacent to the carbonyl group. A peak

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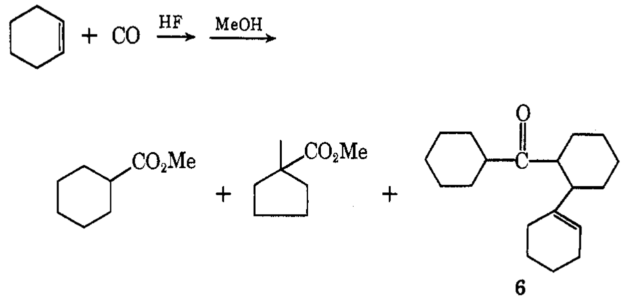
(6) H. Koch, U. S. Patent 2,831,877 (Apr 22, 1958).

(7) K. V. Puzitskii, Ya. T. Eidus, K. G. Ryabovas, and I. V. Guseva, *Dokl. Akad. Nauk SSSR*, **128**, 555 (1959); *Chem. Abstr.*, **54**, 7584 (1960).

Table I
Reaction of 1-Pentene with CO in HF

| Run | HF/Pentene, mol | CO, psig | Pentene/H$_2$O, mol | Temp, °C | Time, hr | Hexane solvent, ml | Yield[a] of C$_6$ acids, % | Selectivity[b] of acids, % | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | DMBA | MVA | EBA |
| 1 | 4.0 | 1000 | 2.4 | 48 | 4 | 0 | 40 | 38 | 28 | 34 |
| 2[c] | 4.0 | 1000 | 2.4 | 48 | 2 | 0 | 33 | 33 | 29 | 38 |
| 3 | 4.0 | 2500 | 2.4 | 48 | 2 | 0 | 29 | 14 | 37 | 49 |
| 4 | 7.5 | 1300 | 1.0 | 48 | 2 | 200 | 49 | 38 | 27 | 35 |
| 5 | 8.0 | 2700 | 0.9 | 10 | 3 | 0 | 37 | 11 | 44 | 45 |
| 6 | 8.0 | 2700 | 0.9 | 10 | 3 | 200 | 43 | 11 | 37 | 52 |
| 7 | 8.0 | 2900 | 0.9 | 10 | 17 | 200 | 56 | 11 | 37 | 52 |
| 8 | 15.0 | 1000 | 0.9 | 45 | 1.5 | 0 | 90 | 36 | 27 | 37 |

[a] Yields are based on distilled C$_6$ carboxylic acids. [b] DMBA = 2,2-dimethylbutyric acid; MVA = 2-methylvaleric acid; EBA = 2-ethylbutyric acid. [c] 2-Pentene was used in place of 1-pentene.



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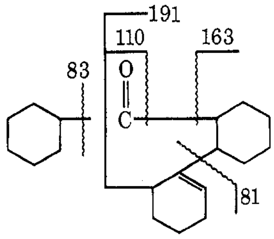
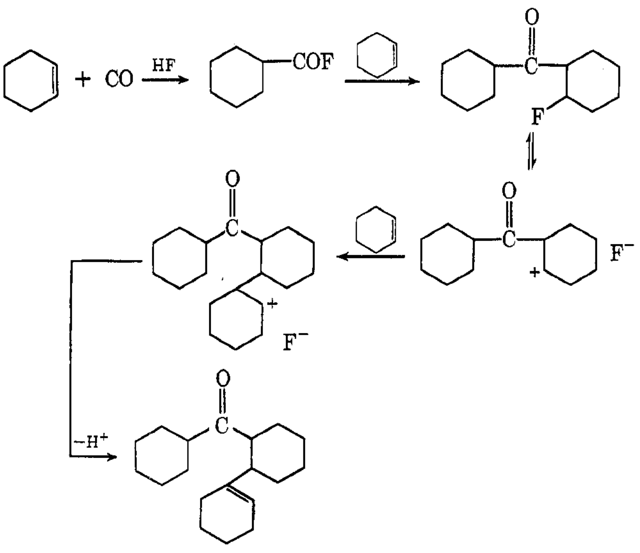
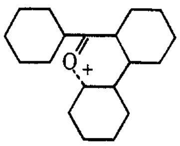
at τ 4.65 indicates the presence of one olefinic proton. The mass spectrum was more indicative in that a parent peak at m/e 274 was obtained (calcd 274) and no other peaks were found in that area. All of the major mass spectral peaks can be explained on the basis of the following scissions.



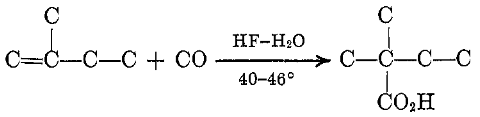
The rationale for formation of the ketone is as shown.



The fact that the oligomerization stops at this point and a fair yield is observed may be due to steric considerations or to an oxonium stabilization of the intermediate carbonium ion of the type shown.

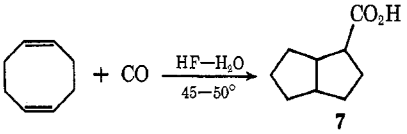


**Miscellaneous Olefins.**—A tertiary olefin, 2-methyl-2-butene, was treated with CO (1000 psig) in 80% aqueous HF to give a 57% yield of 2-methyl-2-butanecarboxylic acid. With tertiary olefins, whose protonation is more facile than that of a secondary olefin, additional water should be present to trap the acyl fluoride as it is formed and to prevent a reverse reaction.[1] Some pivalic and higher acids were also obtained as a result of carbon skeleton fragmentation.



$$\mathrm{C{=}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}C + CO \xrightarrow[40\text{–}46^\circ]{HF\text{–}H_2O} C{-}\underset{\underset{\displaystyle CO_2H}{|}}{\overset{\displaystyle C}{\overset{|}{C}}}{-}C{-}C}$$

On reaction of 1,5-cyclooctadiene and CO (1300 psig) in 90% aqueous hydrogen fluoride, a 17% yield of the transannular product, 2-bicyclo[3.3.0]octane carboxylic acid (7), was isolated.



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Cyclododecene provided a 39% yield of a C$_{12}$-acid mixture distilling at 137–149° (0.4–0.5 mm) which solidified. Recrystallization gave a 17% over-all yield of cyclododecanecarboxylic acid. An olefin, which contains a deeply buried double bond such as that in 7-tetradecene, when treated with 1140 psig CO in 87% aqueous hydrogen fluoride, afforded only a trace of C$_{14}$ acids along with a large amount of a grey-brown but transparent rubbery polymer. If conditions were changed to 3000 psig CO and 94% aqueous HF with a hexane solvent, a 60% distilled yield of tetradecanecarboxylic acids, bp 126–133° (0.05 mm), could be isolated. The individual acids were not separated because of the large number of isomers possible. A mixture of C$_7$–C$_9$ linear olefins with the double bond buried in the chains provided an 84% distilled yield of colorless carboxylic acids, bp 76–86° (0.10 mm), using 1200 psig CO. Similarly, a C$_{10}$–C$_{11}$ fraction of internal olefins under 2600 psig CO gave a 65% yield of carboxylic acids, bp 100–104° (0.15 mm). Yield calculations were based on the amount of each olefin present in the mixture.

## Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord, nmr spectra were run on a Varian A-60 spectrometer, and the mass spectra were obtained on a CEC mass spectrometer, Model 21-110. Product composition of the carboxylic acids was determined on an F & M Model 500 gas chromatograph with a 5-ft, 16.6% Carbowax 20M on 60–80 mesh acid-washed Chromosorb P, programmed at 100–250° at 15° per minute. Capillary columns used were a 150-ft Carbowax 1540 or Apiezon L in conjunction with a Perkin-Elmer Model 900 gas chromatograph.

**Chemicals.**—Caution! When handling anhydrous HF, a face shield, rubber gloves with plastic arm bands, and a protective apron should be worn, using excellent hood facilities. Colorless hydrogen fluoride (99% from Air Products, Inc., Allentown, Pa.) was withdrawn in the liquid phase by inverting the cylinder and taking off liquid HF through a Monel Hoke valve in addition to the cylinder valve. The liquid HF was allowed to drip directly into a polyethylene graduate where it readily condenses as a fuming liquid; it was then poured into a 300-ml Monel transfer bomb. No special precautions were required to exclude moisture or air.

Carbon monoxide (99%) was obtained from Matheson and Co., and the olefins were Phillips pure grade when available. Reference samples of the pure acids were obtained from Baker Chemical Co. and Aldrich Chemical Co.

**Apparatus.**—All reactions were run in a 1-l. Monel magnetically stirred autoclave equipped with a bottom tap. For carbon monoxide pressures of 0–1300 psig, normal cylinder pressure was used. For higher pressures, a Whitey Laboratory Compressor (Model LC-10) was used and the olefin was pumped into the reactor against high pressures with a Whitey Laboratory Feed Pump (Model LP-10).

**General Procedure for Reaction of Olefins with Carbon Monoxide in HF.**—This following description of the reaction is generalized, the variable data having been recorded under the appropriate heading in Table I. A 300-ml Monel bomb was cooled in ice, and addition of water (when used) was followed by the liquid HF. The bomb, capped with a pressure gauge and a dipstick, was pressured with 50–100 psig of carbon monoxide and the contents were blown into the 1-l. reactor. When hexane solvent was employed, this was added next by means of the Whitey pump. The reactor was then pressured with the desired amount of carbon monoxide and heated with circulating water to the specified temperature. The olefin was then pumped into the reactor over a period of 1 hr while being stirred. Stirring was continued for the specified time at the same temperature as the addition. When the reaction was completed, cold water was circulated through the coils and the excess CO pressure was vented into a hood.

Work-up was generally accomplished by pumping 300–350 ml of water, followed by 150 ml of hexane, into the reactor. The contents were stirred for 15 min and allowed to settle. Essentially an extraction of the acid phase was carried out in the reactor. The liquid was then drained into a plastic separatory funnel and the layers were separated. The upper hexane layer was shaken with a NaOH solution to convert the carboxylic acids to the sodium salt; this was followed by two hexane extractions. Removal of the hexane after drying over $MgSO_4$ gave the "upper basic" layer. The NaOH solution was then acidified with sulfuric acid, extracted with hexane (3 × 250 ml), and dried over $MgSO_4$. After removal of the solvent on a Rotavapor, the crude carboxylic acids ("top acid" layer) were distilled and analyzed.

**Reaction of Cyclohexene with Carbon Monoxide and HF at 1000 psig.**—The 1-l. Monel reactor was charged with a mixture of HF (160 g, 8 mol) and $H_2O$ (20 g, 1.1 mol) and pressured to 1000 psig with CO. Cyclohexene (82 g, 1 mol) was pumped into the reactor over a period of 1 hr at 50°. A total uptake of 250 psig of CO was noted after the mixture had been stirred for an additional 2.5 hr at 46–50°. The CO was vented, the reactor was cooled to 20°, 350 ml of $H_2O$ and 200 ml of hexane were pumped into the reactor, and the mixture was stirred for 20 min to extract the acid into the hexane phase. The mixture was drained into plastic separatory funnels and the hexane layer which separated was shaken with a dilute NaOH solution to convert the carboxylic acids into the Na salts. Evaporation of the dried hexane solution gave 4.9 g of neutral materials identified as chiefly self-esters by infrared. The NaOH solution was acidified with concentrated $H_2SO_4$ and extracted with hexane to give 119.5 g (93.5%) of crude, although nearly colorless, carboxylic acids. A small sample was converted to the methyl esters by the method of Metcalfe and Schmitz[8] using $BF_3 \cdot MeOH$ complex obtained from Applied Science Laboratories. By glc analysis, this sample was found to contain 27% of the ring-contracted 1-methylcyclopentyl derivative and 73% of the cyclohexyl product. Distillation of 117.2 g of the free acids through a 15-in. Vigreux column gave 107.2 g (84% yield) of colorless acids, bp 75–87° (0.8–1.2 mm), $n^{20}D$ 1.4598, mol wt, 127.9, neut equiv, 7.67 mequiv/g, and a still pot residue, 8.3 g.

**Reaction of Cyclohexene with Carbon Monoxide and Anhydrous HF Followed by Methanol Addition.**—Hydrogen fluoride (175 g, 8.75 mol) was charged into the 1-l. autoclave and pressured to 100 psig with carbon monoxide. With the temperature maintained at 22–23° by circulating tap water, cyclohexene (82 g, 1 mol) was pumped into the reactor at 1.0–1.8 ml/min. During this time, the pressure fell from 1040 to 820 psig; total addition time was 65 min. After an additional 1 hr of stirring, the CO pressure was released and the HF (147 g) was removed *in vacuo*. Methanol (200 ml) was pumped into the reactor and the mixture was heated with warm water (45°) and stirred for 2 hr. The mixture was drained from the reactor, poured on ice, neutralized with 40% NaOH, and extracted with hexane (3 × 250 ml). Removal of the hexane on a Rotavapor after drying over $MgSO_4$ left 97.7 g of a liquid. The aqueous layer was acidified with concentrated $H_2SO_4$ to pH 3.0 and extracted with hexane to give 6.2 g of liquid. The extract from the basic solution was distilled through a 15-in. vacuum-jacketed Vigreux column. Considerable foaming occurred and finally 80.2 g of a distillate was obtained which was redistilled as shown in Table II.

TABLE II

| Cut | Bp, °C (13 mm) | Wt, g | $n^{20}D$ |
|---|---|---|---|
| 1 | 58–61 | 42.6 | 1.4413 |
| 2 | 61–130 | 1.6 | |
| 3 | 130–180 | 6.9 | |
| 4 | 180–200 | 21.8 | 1.5117 |
| Pot residue | | 6.0 | |

Cut 1 represents the cyclic methyl esters with the composition being 91% methyl cyclohexanoate and 9% methyl 1-methylcyclopentanoate. The yield of esters normalized to the initial weight is 37%.

Cut 4 was redistilled at 129–130° (0.15 mm), $n^{20}D$ 1.5117, and identified as 2-(cyclohexenyl)cyclohexyl cyclohexyl ketone. See discussion for the nmr and mass spectral data.

*Anal.* Calcd for $C_{19}H_{30}O$: C, 83.28; H, 11.04; mol wt, 274. Found: C, 82.75; H, 10.94; mol wt, 278 (osmometry).

**7-Tetradecene with Carbon Monoxide–HF–$H_2O$ at 3000 psig.**—The 1-l. reactor was charged with 160 g (8 mol) of HF, 10 g (0.55 mol) of water, and 200 ml of *n*-hexane and pressured to about 2800 psig with CO. The temperature was maintained 20–22° with circulating water. 7-Tetradecene (78.4 g, 0.40 mol) diluted with an equal volume of *n*-hexane was pumped in the reactor over a period of 1 hr, which raised the pressure to 3000 psig. An additional 50 ml of hexane was added and the mixture was stirred for 4 hr at 20–30°. The CO was vented and 350 ml of water and 150 ml of hexane were charged into the reactor and stirred. The colorless solution was drained into a plastic container and the upper hexane layer was shaken with a NaOH solution. After drying over $MgSO_4$, removal of the hexane gave 21.8 g of neutral components. The NaOH solution was acidified with $H_2SO_4$ and extracted with hexane to give 64.4 g of colorless acids. Distillation of 61.2 g of the acids gave essentially one cut, 54.8 g (0.23 mol, 58% yield), bp 126–133° (0.05 mm), $n^{20}D$ 1.4450, of colorless $C_{14}$ acids with only 1.0 g of residue.

*Anal.* Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.47; mol wt, 242. Found: C, 74.54; H, 13.08; mol wt, 237; neut equiv, 4.24 mequiv/g.

**Carboxylation of $C_{10}$–$C_{11}$ Mixture of Internal Olefins.**—The

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(8) L. D. Metcalfe and A. A. Schmitz, *Anal. Chem.*, **33**, 363 (1961).

olefins employed were a mixture of internal olefins and possessed the following composition: $C_9$, 10.2; $C_{10}$, 50.6; $C_{11}$, 38.1; $C_{12}$, 1.0; average mol wt, 142.4. The autoclave was charged with 160 g (8 mol) of HF and 10 g (0.55 mol) of $H_2O$ and pressured to 2500 psig with CO. The temperature was 45–50° and 45 min were required to pump in 70 g of olefins used. Distillation of 140 g of HF left a light-colored residue which was poured on ice and made basic with NaOH.

Extraction with hexane gave 3.7 g of neutrals. Acidification of the aqueous solution after hexane extraction gave 69.3 g of crude acids. Distillation of 66.8 g gave essentially one cut weighing 59.1 g (63% yield) of colorless acids, bp 100–104° (0.15 mm), $n^{20}D$ 1.4380, with 2.2 g of heavy residue remaining.

*Anal.* Found: C, 71.44; H, 12.18; mol wt, 185; neut equiv, 5.18 mequiv/g.

**Carboxylation of 1,5-Cyclooctadiene with CO–HF–$H_2O$.**—The 1-l. Monel autoclave was charged with 215 g (10.8 mol) of HF and 25 g (1.4 mol) of $H_2O$ and pressured to 1300 psig with CO. 1,5-Cyclooctadiene (108 g, 1 mol) was added over a period of 2 hr to the mixture heated at 45–50°. After stirring for an additional 1 hr, the CO was vented and the reactor was cooled. HF (176 g) was removed by distillation and the residue was poured on ice and made basic with NaOH followed by extraction with $CHCl_3$. The bottom $CHCl_3$ layer was filtered and dried over $MgSO_4$. An intermediate red-brown layer was very viscous and seemed insoluble in both $CHCl_3$ and $H_2O$. The top aqueous layer was reextracted with $CHCl_3$ and then acidified with $H_2SO_4$. Removal of the $CHCl_3$ from the basic extract left 37.7 g of a viscous liquid which was probably the same as the intermediate layer. The acidified layer was extracted with *n*-hexane to give 42.6 g of acids after drying over $MgSO_4$. Distillation of 37.4 g through a 6-in. Vigreux column provided 22.7 g of a heart cut. Redistillation gave the pure acid, bp 91–93° (0.2 mm), $n^{20}D$ 1.4867 [lit.[9] bp 132° (25 mm)]. The nmr spectrum supported the assigned structure, **7**, a singlet at $\tau$ −2.7 ($RCO_2H$) and a multiplet at $\tau$ 7–9 in a ratio of 13:1 with no evidence for olefinic protons.

*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.15; mol wt, 154. Found: C, 70.00; H, 9.08; mol wt, 152; neut equiv, 6.57 mequiv/g.

**Carboxylation of Cyclododecene with CO–HF.**—The autoclave was charged with water (10 g) and HF (160 g) and pressured to 2300 psig CO at 45–50°. Cyclododecene (50.4 g, 0.30 mol) dissolved in 100 ml of cyclohexane was added over a period of 40 min. After a reaction time of 3 hr, the reactor was cooled, the CO was vented, and 350 ml of $H_2O$ followed by 150 ml of hexane was added to the autoclave. The contents were drained into a plastic separatory funnel. The upper organic layer was shaken with 10% NaOH to form carboxylic acid salts. Evaporation of the remaining organic layer provided 15.5 g of neutrals. Acidification of the aqueous layer with $H_2SO_4$ and chloroform extraction gave 42 g of nearly colorless acids. Distillation provided 24.8 g of a heart cut, bp 137–149° (0.3–0.5 mm), of acids which solidified on cooling. Recrystallization (hexane) gave cyclododecanecarboxylic acid, mp 97–98° (lit.[10] mp 97.5°).

**Registry No.**—**6**, 34402-87-4; **7**, 7403-22-7; HF, 7664-39-3; CO, 630-08-0; 1-pentene, 109-67-1; cyclohexene, 110-83-8; methyl cyclohexanoate, 4630-82-4; 7-tetradecene, 10374-74-0; 1,5-cyclooctadiene, 111-78-4; cyclododecene, 1501-82-2.

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[9] G. Pregaglia and G. Gregorio, *Chim. Ind.* (*Milan*), **45**, 1065 (1963).

[10] G. Bo, P. Perras, and Y. Colleuille (to Rhone-Poulenc), French Patent 1,286,803 (Mar 9, 1962); *Chem. Abstr.*, **57**, 14967 (1962).

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# The Tiffeneau–Demjanov Reaction on Phenyl-Fused Cyclopentyl Systems

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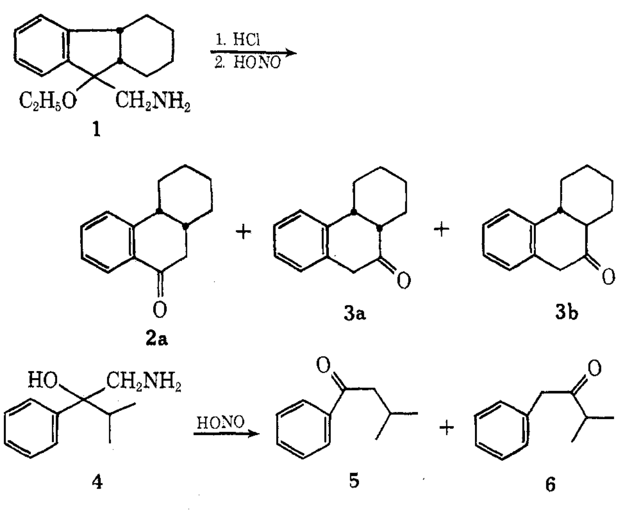
The diastereomeric amine hydrochlorides **10a** and **10b** were prepared and their reactions with nitrous acid were studied. Change of stereochemistry at C-9 in **10** is not a significant factor affecting aryl to alkyl migration in this system; however, it is noted that the ketone product ratios changed markedly changing the ethoxy group at C-9 (in **1**) to hydroxy (**10a** or **10b**).

The Tiffeneau–Demjanov reaction (the action of nitrous acid on $\beta$-amino alcohols) of phenyl-fused cyclopentyl systems, in which the migration may be by either the phenyl group or alkyl group, has not heretofore been investigated. A modified Tiffeneau–Demjanov reaction on one diastereomer of the $\beta$-amino ether **1** (Scheme I) gave an unusually large ratio of alkyl migration product **2a** to aryl migration product **3**[1] (ratio **2a**/**3** = 1/0.2–0.9) as compared to the analogous monocyclic system **4** (ratio **5**/**6** = 1/31). The observed preferential alkyl migration was attributed to the geometric requirement for phenyl migration. In **1** the phenyl nucleus cannot rotate to the position assumed to be most favorable for migration because of the constraint inherent in the fused system.[1] An alternate explanation, based on dependence of stereochemistry at C-9, was not eliminated, however, since attempts to prepare the other diastereomer of **1** and the two diastereomers **10a** and **10b** were unsuccessful.[1]

SCHEME I



This report describes preparation of the diastereomeric amine hydrochlorides **10a** and **10b**, and considers in greater detail factors which affect product ratios in the Tiffeneau–Demjanov reaction in these fused systems.

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[1] W. E. Parham and L. J. Czuba, *J. Amer. Chem. Soc.*, **90**, 4030 (1968).