

A Comparison of the Effectiveness of Sulphuric Acid and Trifluoromethanesulphonic Acid in Koch Carboxylation Reactions

By Brian L. Booth* and Teymour A. El-Fekky, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Trifluoromethanesulphonic acid has been found to be far superior to 95% sulphuric acid for the carboxylation of olefins, alcohols, and esters with carbon monoxide at atmospheric pressure. This is attributed to the higher acidity of $\text{CF}_3\text{SO}_3\text{H}$ and also the higher solubility of carbon monoxide in this acid. At higher carbon monoxide pressures the difference in behaviour of the two acids is much less marked as, under these conditions, the carbon monoxide concentration is not a limiting factor.

TRIFLUOROMETHANESULPHONIC ACID ('triflic acid') has been acclaimed as one of the strongest of all known monoprotic organic acids.¹ To date, however, most of the interest in the chemistry of this acid and its derivatives has centred around the remarkable efficiency of the triflate anion as a leaving group,²⁻⁴ particularly in solvolysis,⁵⁻⁸ alkylation,^{9,10} acylation,^{11,12} and nitration^{13,14} reactions, and in the use of triflamides in organic synthesis.¹⁵ With the exception of reports on the use of triflic acid for the isomerisation and cracking of hydrocarbons,¹⁶⁻²¹ and as a catalyst for the Fries rearrangement,²² there is little information about the effect of this acid in other reactions of synthetic importance. Triflic acid has several advantages over other strong acids in that it is non-oxidising, and has high thermal stability and resistance to oxidation and reduction. Moreover, unlike sulphuric acid, it does not give electrophilic substitution products with aromatic hydrocarbons. Perhaps the most important advantage, when compared with other 'super acids' such as FSO_3H and $\text{FSO}_3\text{H-SbF}_5$, is that it can be regenerated almost quantitatively by precipitation as its barium salt, followed by treatment of the salt with 100% sulphuric acid.

We now report the results of an investigation into the use of triflic acid as a catalyst for the Koch carboxylation

of olefins, alcohols, and esters, and discuss reasons for the differences in yields and product distribution from those obtained under similar conditions with the conventional catalyst, 95% sulphuric acid.

RESULTS AND DISCUSSION

Slow addition of a dilute solution of cyclohexane in CCl_4 to a stirred solution of 95% sulphuric acid at 0 °C while bubbling carbon monoxide through the solution gave a 52% yield of a mixture of 1-methylcyclopentane-carboxylic acid (I), cyclohexanecarboxylic acid (II), and polymeric acids of molecular formula $\text{C}_{13}\text{H}_{22}\text{O}_2$ (III) in the ratios 9 : 1 : 23.3 (see Table 1). The other products of this reaction, formed in 31% yield, were neutral compounds, shown by g.l.c.-mass spectrometry to be mainly hydrocarbons, together with small amounts of cyclohexanol, and cyclohexyl and methylcyclopentyl esters, such as *cyclo*- $\text{C}_6\text{H}_{11}\text{CO}_2\text{C}_6\text{H}_{11}$ -*cyclo*, *cyclo*- $\text{MeC}_5\text{H}_8\text{CO}_2\text{C}_6\text{H}_{11}$ -*cyclo*, and *cyclo*- $\text{MeC}_5\text{H}_8\text{CO}_2\text{C}_5\text{H}_8\text{Me}$ -*cyclo*. The concentration of the sulphuric acid used in this reaction is a critical factor. When this was reduced to 85% the products consisted almost entirely of the hydration product cyclohexanol, with only traces of carboxylic acids.

Under similar conditions, but using 95% triflic acid, the yield of carboxylic acids rose to 88%, and there was

TABLE I
Carboxylation reactions at atmospheric pressure^a

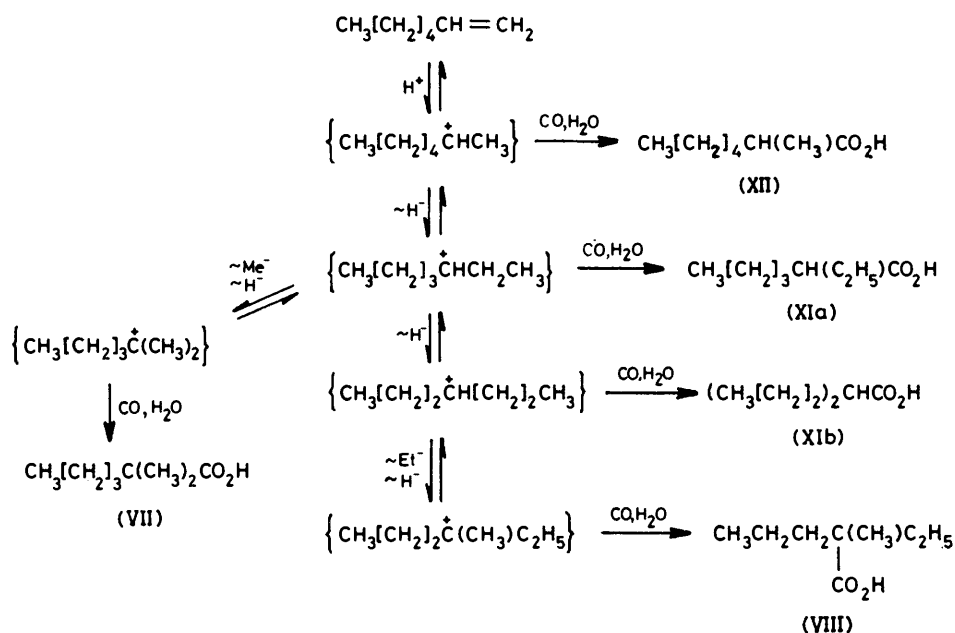
Substrate	Acid catalyst	Carboxylic acids (%)	Neutral products (%)	Monomeric acids (% of total)	Polymeric acids (% of total)
Cyclohexene	H_2SO_4	52	31	(I) 27, (II) 3	(III) 70
	$\text{CF}_3\text{SO}_3\text{H}$	88	4	(I) 68, (II) 7	(III) 25
	$\text{H}_2\text{SO}_4\text{-HCO}_2\text{H}^c$	60	10	(I) + (II) 65	(III) 35
Cyclohexanol	H_2SO_4	43	39	(I) 21, (II) 5	(III) 74
	$\text{CF}_3\text{SO}_3\text{H}$	86	6	(I) 64, (II) 9	(III) 27
	H_2SO_4	42	10	(I) 25, (II) 4	(III) 71
Cyclohexyl tosylate	$\text{CF}_3\text{SO}_3\text{H}$	88	1	(I) 74, (II) 9	(III) 17
	H_2SO_4	26	24	(IV) ??	(V) 17, (VI) 72
	$\text{CF}_3\text{SO}_3\text{H}$	55	19	(IV) 37	(V) 15, (VI) 48
Cyclopentene	H_2SO_4	68	11	(VII) 30, (VIII) 53 ^b	(IX) 17
	$\text{CF}_3\text{SO}_3\text{H}$	91	1	(VII) 43, (VIII) 56 ^b	(IX) 11
	H_2SO_4	50	16	(X) 42	
2-Methylpropan-1-ol	$\text{CF}_3\text{SO}_3\text{H}$	74	1	(X) 93	

(I) 1-Methylcyclopentanecarboxylic acid, (II) cyclohexanecarboxylic acid, (III) $\text{C}_{13}\text{H}_{22}\text{O}_2$ acids, (IV) cyclopentanecarboxylic acid, (V) *cis*-decalin-4a-carboxylic acid, (VI) *trans*-decalin-4a-carboxylic acid, (VII) 2,2-dimethylhexanoic acid, (VIII) 2-ethyl-2-methylpentanoic acid, (IX) $\text{C}_{15}\text{H}_{30}\text{O}_2$ acids, (X) 2,2-dimethylpropanoic acid.

^a Ratio of 95% acid to organic substrate = 8 : 1; CCl_4 solvent (0.5M-solution); addition period 2 h. ^b Mixture also contained traces of 2-ethylhexanoic acid (XIa) and 2-propylpentanoic acid (XIb) which could not be separated. ^c 98% H_2SO_4 (800 mmol), HCO_2H (74 mmol) in CCl_4 solvent at -5 to 0 °C, and cyclohexene (100 mmol) and HCO_2H (200 mmol) added over 1 h; the ratio of (I) to (II) was not determined.

only 4% of neutral by-products (see Table 1). The ratios of the acid products (I) : (II) : (III) (9.8 : 1 : 3.5) represent a considerable increase in the amount of the monomeric acids at the expense of the polymeric acid products. These results with triflic acid compare very favourably with results obtained using the Koch-Haaf procedure²³ in which carbon monoxide is generated *in situ* by the addition of 98% sulphuric acid to anhydrous formic acid. With cyclohexene, in our hands, this gave a ratio of total monomeric acids [(I) + (II)] to polymeric acids (III) of 1.85 : 1, to be compared with 3.08 : 1 using triflic acid. A very similar pattern of results was obtained using cyclohexanol and cyclohexyl tosylate. In both cases the use of triflic acid leads to a higher total acid yield, and a consistently higher ratio of monomeric acid to polymeric acid products in comparison with the

cyclopentene were surprisingly low in comparison with those from cyclohexene, and even with triflic acid appreciable amounts of neutral products and polymeric carboxylic acids were obtained. This appears to be a peculiarity of the cyclopentyl ring system, since previous reports of the carboxylation of cyclopentene and cyclopentanol under Koch-Haaf conditions quote only 6 and 26% yields, respectively, of carboxylic acids.²³ Further, carboxylation of cyclopentene with sulphuric acid and a CO pressure of 76 atm is reported to give only a 24% yield of acids.²⁴ The major polymeric acid products in all these reactions are *cis*- and *trans*-decalin-4a-carboxylic acid, arising by carbonylation of the tertiary decalylium ion formed by a particularly ready ring expansion of the intermediate produced on reaction of cyclopentylum ion with cyclopentene.

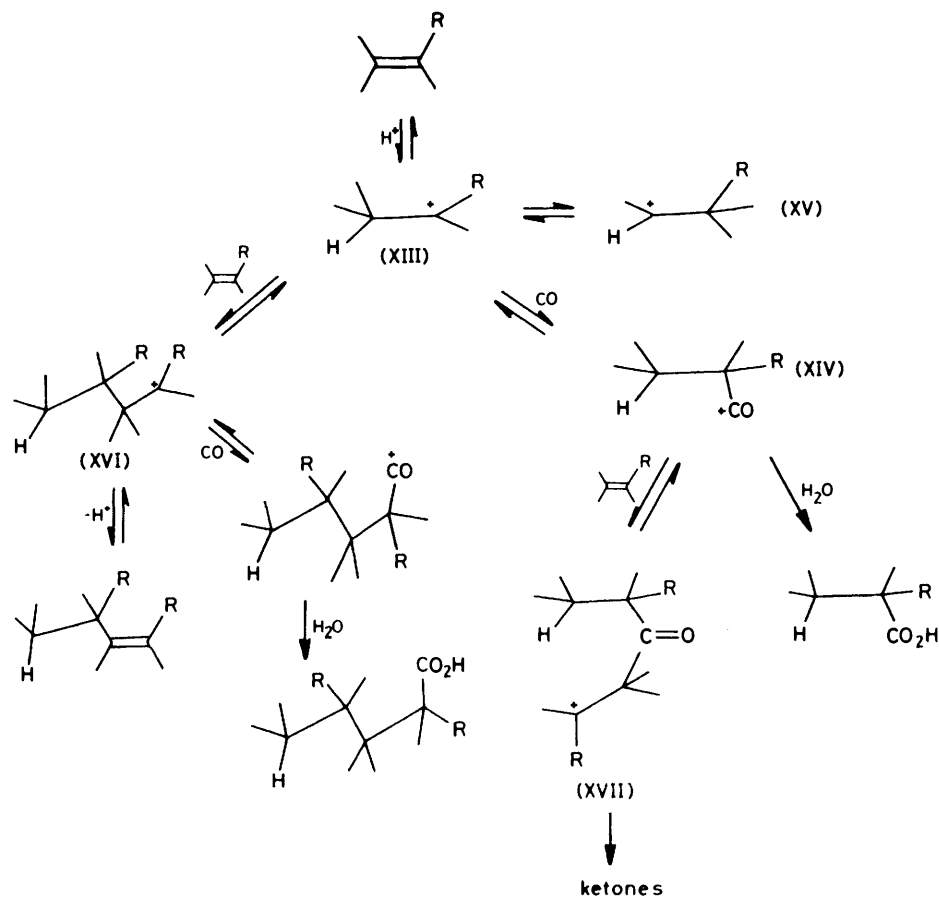


SCHEME 1

same reactions in 95% sulphuric acid. There are some slight variations in product yields, but, within experimental error, the nature of the leaving group appears to have little influence on the product distribution (see Table 1).

Extension of these triflic-acid-catalysed carboxylation reactions to cyclopentene, hept-1-ene, and 2-methylpropan-2-ol again resulted in a significant improvement in the yields of the corresponding monomeric acids, and reduction in the amounts of neutral and polymeric acid by-products. The reaction of hept-1-ene is complicated by the fact that the initially formed 1-methylhexylium ion undergoes a number of rapid intramolecular rearrangements leading to five possible monomeric acid products (see Scheme 1). Of these, only two, namely 2,2-dimethylhexanoic acid (VII) and 2-ethyl-2-methylpentanoic acid (VIII) are major products under atmospheric pressure. The yields of carboxylic acids from

The improvement in the ratio of monomeric acids to polymeric acids and neutral products brought about by using triflic acid under atmospheric-pressure carboxylation conditions can, in part, be attributed to its high acid strength in comparison with sulphuric acid. A general mechanism for the carboxylation of an olefin is given in Scheme 2. One effect of the increased acid strength will be to increase the concentration of the cation (XIII) leading to greater rates of both carbonylation [to form (XIV)] and isomerisation to the cation (XV). As a consequence, the concentration of free olefin will be considerably reduced, resulting in lower rates for the competing reactions leading to polymeric acids and neutral hydrocarbons [*via* (XVI)], and ketonic neutral products [*via* (XVII)]. Another factor, which is frequently the limiting factor in Koch carboxylation reactions carried out with 1 atm of carbon monoxide, is the CO concentration in solution. Available inform-



SCHEME 2

ation on the solubilities of CO in 'super acid' media suggests that there can be large variations depending upon the acid system. So, for example, a solubility of 0.04 mol l^{-1} (896 ml) has been reported²⁵ in HF-SbF_5 at 20°C and 160 mmHg pressure, compared with only 0.004 mol l^{-1} (90 ml) in $\text{FSO}_3\text{H-SbF}_5$ under the same conditions. An earlier report²⁶ suggests an even lower solubility of only 10 ml l^{-1} in $\text{FSO}_3\text{H-SbF-SO}_3$ at 20°C . In our hands, the solubility of carbon monoxide in 95% triflic acid, measured at 27°C and 774 mmHg by a standard procedure,²⁷ was found to be 155 ml l^{-1} , to be compared with a value of 21 ml l^{-1} for 95% sulphuric acid under the same conditions. This seven-fold increase in CO concentration leads to higher rates of

carbonylation of the carbocation intermediates, and this, together with the effect of the higher acid strength, explains the improved yields of monomeric carboxylic acids in comparison with the sulphuric acid system.

It was of interest, also, to examine the effect of changing the ratio of triflic acid to organic substrate upon the product distribution. A series of experiments was carried out with cyclohexene and 1 atm of carbon monoxide at room temperature, in which the triflic acid : cyclohexene ratio was varied over the range 1 : 1 to 12 : 1. The results (Table 2) are entirely consistent with the effect expected on the basis of the argument put forward earlier. So, for example, as the ratio acid : cyclohexene increases both the proportion of total

TABLE 2

The effect of the ratio of 95% triflic acid : cyclohexene on the product distribution from carbonylation at atmospheric pressure^a

Ratio	Carboxylic acids	Neutral products (%)	Distribution of acids (% of total)			Ratio (I) : (II)
			(I)	(II)	(III)	
1 : 1	11	72	52	17	31	3.1
2 : 1	52	23	44	14	42	3.1
4 : 1	82	7	62	13	25	4.8
8 : 1	88	4	68	7	25	9.7
12 : 1	92	4	85	5	10	17.0

(I) 1-Methylcyclopentanecarboxylic acid, (II) cyclohexanecarboxylic acid, (III) $\text{C}_{13}\text{H}_{22}\text{O}_2$ acids.

^a CCl_4 solvent (0.5M-solution); addition period 2 h.

carboxylic acids to neutral products, and the proportion of monomeric acids to polymeric acids increases. It is interesting that as the acid : cyclohexene ratio increases then the ratio (I) : (II) within the monomeric acids also increases significantly. This again illustrates that under these atmospheric-pressure conditions the carbon monoxide concentration in solution is a limiting factor. Even with a low acid : cyclohexene ratio the rate of isomerisation of the cyclohexylium ion to the methylcyclopentylum ion is much greater than its rate of carbonylation to $cyclo-C_6H_{11}^+CO$. Nevertheless, at these lower acid concentrations the ratio $[cyclo-C_6H_{11}^+] : [CO]$ is such that the rate of carbonylation of this cation is appreciable. As the ratio acid : cyclohexene increases there will be an increase in $[cyclo-C_6H_{11}^+]$ concentration, with a corresponding increase in the rates of both isomerisation and carbonylation. However, the carbonylation reaction, being bimolecular, is also governed by the

isomerisation to $cyclo-MeC_5H_9^+$. The improved solubility of CO in triflic acid in comparison with sulphuric acid still has some influence even at this high pressure as evidenced by the lower ratio (1 : 3.2) of (I) to (II) obtained with sulphuric acid under comparable conditions.

The effect of the CO concentration is further illustrated by the reaction of hept-1-ene. With a high pressure of CO the combined yield of 2-propylpentanoic acid (XIb) and 2-ethylhexanoic acid (XIa) increases from only traces at atmospheric pressure to 30% (sulphuric acid) and 62% (triflic acid) respectively, at the expense of the tertiary acids (VII) and (VIII). Similarly, 2-methylheptanoic acid (XII), which could not be detected in the products of the atmospheric pressure reactions, is formed in low yields at the higher CO pressure. In these reactions the isomerisation of the initially formed cation $CH_3[CH_2]_4\dot{C}HCH_3$ to $CH_3[CH_2]_3\dot{C}HCH_2CH_3$ and

TABLE 3
Carboxylation reactions under 90 atm CO pressure^a

Substrate	Acid catalyst	Carboxylic acids (%)	Neutral products (%)	Monomeric acids (% of total)	Polymeric acids (% of total)
Cyclohexene	H ₂ SO ₄	78	3	(I) 24, (II) 76	
	CF ₃ SO ₃ H	83	tr ^b	(I) 8, (II) 92	
Cyclohexanol	H ₂ SO ₄	78	6	(I) 24, (II) 76	
	CF ₃ SO ₃ H	90	1	(I) 8, (II) 92	
Cyclohexyl tosylate	H ₂ SO ₄	81	1	(I) 24, (II) 76	
	CF ₃ SO ₃ H	90	tr ^b	(I) 9, (II) 91	
Cyclopentene	H ₂ SO ₄	65	2	(IV) 97	(V) I, (VI) 2
	CF ₃ SO ₃ H	76	tr ^b	(IV) 99	(V) 0.3, (VI) 0.7
Hept-1-ene	H ₂ SO ₄	82	1	(VII) 27, (VIII) 41	
	CF ₃ SO ₃ H	88	1	(XI) 30, (XII) 2 (VII) 15, (VIII) 18 (XI) 62, (XII) 5	

^a Ratio of 95% to organic substrate = 8 : 1, CCl₄ solvent (0.5M-solution); addition period 1 h. ^b tr = Trace.

(I) 1-Methylcyclopentanecarboxylic acid, (II) cyclohexanecarboxylic acid, (IV) cyclopentanecarboxylic acid, (V) *cis*-decalin-4a-carboxylic acid, (VI) *trans*-decalin-4a-carboxylic acid, (VII) 2,2-dimethylhexanoic acid, (VIII) 2-ethyl-2-methylpentanoic acid, (XI) inseparable mixture of 2-propylpentanoic acid (XIa) and 2-ethylhexanoic acid (XIb), (XII) 2-methylheptanoic acid.

CO concentration. Although the CO concentration increases with increase in the acid : cyclohexene ratio the increase is insufficient to compensate for the increase in rate of isomerisation of $cyclo-C_6H_{11}^+$ to $cyclo-MeC_5H_9^+$.

Very different results are obtained when these carbonylation reactions are carried out under a high pressure of carbon monoxide (see Table 3). When the CO pressure is high there is little formation of polymeric acids and the yield of neutral products is reduced. Moreover, the yields of monomeric carboxylic acids obtained with sulphuric acid are now comparable to those from the triflic acid reactions. Under these conditions the concentration of CO in both sulphuric acid and triflic acid is sufficiently high for this not to be such a limiting factor in these carbonylation reactions. This can be seen clearly in the ratio of the monomeric acids (I) : (II) from cyclohexene. Comparison of the triflic-acid-catalysed reactions shows that this ratio changes from 9.7 : 1 for the atmospheric pressure reaction to 1 : 10.8 under high pressure conditions. When the concentration of CO is high the rate of carbonylation of the cyclohexyl cation is now much greater than the rate of

$CH_3[CH_2]_2\dot{C}H[CH_2]_2CH_3$ (see Scheme 1) occurs by a very rapid hydride ion migration (ΔG^\ddagger ca. 5—6 kcal mol⁻¹)²⁸ and even with high CO concentrations the lower rate of carbonylation (ΔG^\ddagger ca. 7—8 kcal mol⁻¹)²⁹ of these cations can not compete very effectively with these fast isomerisation reactions. However, the rates of isomerisation of these intermediates to the tertiary carbocations $CH_3[CH_2]_3\dot{C}Me_2$ and $CH_3[CH_2]_2\dot{C}MeEt$ are much lower (ΔG^\ddagger ca. 13—16 kcal mol⁻¹)²⁸. Although carbonylation is not competitive with these isomerisation reactions under the [CO]-limiting conditions operating at atmospheric pressure, at higher CO pressures, and especially in triflic acid, the rates of carbonylation of the secondary carbocations leading to products (XII) and (XIa and b) are now comparable to the rates of isomerisation to the tertiary carbocations.

EXPERIMENTAL

I.r. spectra were recorded either on a Perkin-Elmer Infracord 137 or a Perkin-Elmer 735 spectrophotometer, and ¹H n.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer R10 or R20 spectrometer. Mass spectra

were obtained using an A.E.I. MS 902 mass spectrometer. G.l.c. analyses were carried out using a Pye series 104 dual F10 gas chromatograph (5 ft \times $\frac{1}{8}$ in column packed with 10% FFAP on Celite). The trifluoromethanesulphonic acid was purified by distillation immediately before use.

General Procedure for Atmospheric Pressure Carboxylation Reactions.—The acid [95% triflic acid (120.0 g, 114.0 mmol) prepared by addition of anhydrous acid (114.0 g) to ice (6.0 g), or 95% sulphuric acid (78.4 g, 800 mmol) obtained by addition of 98% sulphuric acid (76.0 g) to ice (2.4 g)] was placed in a flask fitted with stirrer, gas inlet and outlet, and separating funnel. The flask was cooled to 0 °C and a continuous stream of dry carbon monoxide gas was passed through the solution for 15 min with vigorous stirring. A solution of organic reactant (100 mmol) in CCl_4 (190 ml) was slowly added dropwise to the stirred solution over 2 h while the flow of CO gas was maintained. The mixture was then allowed to warm to room temperature, and stirring, with gas bubbling, was continued for a further hour. The mixture was then poured into a separating funnel containing iced water (200 g). After shaking vigorously the carbon tetrachloride layer was separated, and the aqueous layer was extracted with a further portion (50 ml) of CCl_4 . The combined organic extracts were washed successively with aqueous KOH (1 \times 50 ml and 1 \times 25 ml), and water, before drying (Na_2SO_4). Removal of the solvent gave the 'neutral products' which were then analysed by g.l.c. The combined alkaline extracts were washed with light petroleum (b.p. 60–80 °C), and then acidified to pH 3 with conc. HCl to give the 'acid products' as an oil or emulsion. These were extracted with CCl_4 , and the extracts were dried (Na_2SO_4), and filtered, before removal of the solvent to give a residue which was analysed by g.l.c.

Details of the individual experiments are given in Tables 1 and 2.

General Procedures for High-pressure Carboxylation Reactions.—These reactions were carried out in a 100 ml stainless steel autoclave fitted with a 'Magnadrive' stirrer head, and connected to a stainless steel Pressure Products Ltd 'Linejector 200' high pressure syringe.

The acid [95% sulphuric acid (26.1 g, 266 mmol), or 95% triflic acid (40.0 g, 266 mmol)] was placed in the autoclave, which was then connected to the high-pressure syringe containing a solution of the organic reactant (33.3 mmol) in CCl_4 (28.5 ml). The equipment was then purged with nitrogen before pressurising to 90 atm with carbon monoxide. The contents of the syringe were then added at 28.5 ml h^{-1} with vigorous stirring. Stirring was continued for a further 1 h, before venting the autoclave and pouring the contents into iced water. The work-up procedure thereafter was as described in the preceding section; details of individual experiments are given in Table 3.

Product Analysis and Identification.—(a) *Reactions of cyclohexene, cyclohexanol, and cyclohexyl tosylate.* G.l.c. analysis of the neutral products from these reactions indicated several components (in some cases up to 30). Of these, only cyclohexanol, cyclohexyl 1-methylcyclopentanecarboxylate, and cyclohexyl cyclohexanecarboxylate could be positively identified by comparison of retention times with those of authentic samples. The amounts of monomeric acids, 1-methylcyclopentanecarboxylic acid (I) and cyclohexanecarboxylic acid (II), obtained in these reactions were determined by quantitative g.l.c. analysis, by calibration with authentic samples. The polymeric acids were shown by microanalysis in each case to have the empirical

formula $\text{C}_{13}\text{H}_{22}\text{O}_2$, and g.l.c.–mass spectrometric analysis showed the presence of at least four isomers.

(b) *Reactions of cyclopentene.* The neutral products from these reactions were found by g.l.c. to contain at least 20 components, of which only cyclopentanol, cyclopentyl cyclopentanecarboxylate, and the cyclopentyl esters of *cis*- and *trans*-decalin-4a-carboxylate could be identified, by comparison of their retention times with those of authentic samples. The three components of the acid fraction, namely cyclopentanecarboxylic acid and *cis* and *trans*-decalin-4a-carboxylic acid were analysed quantitatively by g.l.c., using samples previously isolated by preparative g.l.c. and identified by i.r. spectroscopy and mass spectrometry.

(c) *Reactions of hept-1-ene.* The neutral products were shown by g.l.c. to consist of at least five major components but these were not identified. The acid products were fractionated into a C_8 fraction, b.p. 103–106 °C at 13 mmHg and a high-boiling viscous residue shown by g.l.c. to contain several compounds which analysed for dimeric carboxylic acids of molecular formula $\text{C}_{15}\text{H}_{30}\text{O}_2$. The C_8 acid fraction was analysed by comparison of g.l.c. retention times with those of authentic samples and was found to contain 2,2-dimethylhexanoic acid, 2-ethyl-2-methylpentanoic acid, 2-propylpentanoic acid, and 2-ethylhexanoic acid.

(d) *Reactions of 2-methylpropan-2-ol.* The acid products from the reaction with sulphuric acid at atmospheric pressure consisted of 17 components, of which 2,2-dimethylpropanoic acid (identified by comparison of its retention time with that of an authentic sample) accounted for only 42% of the total. The product from the triflic acid reaction under similar conditions consisted of only 6 components, of which 2,2-dimethylpropanoic acid accounted for 93%.

Procedure for Regeneration of Triflic Acid.—Combined aqueous solutions of triflic acid were washed with light petroleum (b.p. 60–80 °C) to remove any traces of organic impurities, before neutralising with barium carbonate. Active charcoal (*ca.* 1 g l^{-1}) was added and the suspension was stirred for 5 min, and after filtration gave an almost colourless filtrate. This was concentrated by evaporation of the water until a saturated solution of the barium salt was obtained. This, on cooling, gave a dense suspension which was filtered off. Concentration of the filtrate gave a further crop of barium triflate, and by repeating this procedure several times it was possible to recover the triflic acid as barium triflate in almost quantitative yield. The combined crops were dissolved in acetone; the solution was filtered to remove any excess of barium carbonate, and the solvent was then evaporated off to give barium triflate, which was dried in a vacuum oven at 100 °C over *ca.* 2 days. It is essential that the barium triflate is absolutely dry as any trace of residual water leads to the formation of $\text{CF}_3\text{-SO}_3\text{H}\cdot\text{H}_2\text{O}$ with consequent decrease in the yield of anhydrous acid.

The dry barium triflate was placed in a 2-necked flask, and 100% sulphuric acid (prepared by addition of a calculated amount of 20% oleum to 98% sulphuric acid) was added. The apparatus was set for distillation under reduced pressure under nitrogen and on gentle heating over 1 h triflic acid distilled over as a colourless liquid, b.p. 67–75 °C at 15 mmHg. Liquid distilling above this temperature, *i.e.* between 75 and 84 °C at 15 mmHg, usually contained an appreciable amount of triflic acid monohydrate, and this was put aside for later regeneration.

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