Formylation and Acylation Reactions Catalysed by Trifluoromethanesulphonic Acid

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Regioselective formylation of toluene, *m*- and *p*-xylene, and mesitylene has been achieved by carbonylation in trifluoromethanesulphonic acid at CO pressures of 90—125 atm. In the case of cumene, the formylation reaction is in competition with disproportionation to form di- and tri-isopropylbenzenes, leading to a complex product mixture. Slow addition of cyclohexene or cyclopentene to a mixture of benzene and CF_3SO_3H under a high CO pressure affords 4-cyclohexylbenzaldehyde and 4-cyclopentylbenzaldehyde in 34% and 33% yields, respectively, while 2-methylbut-1-ene gives 2,2,3-trimethylindanone (39%) under similar conditions. When cyclohexene is mixed with the acid under carbon monoxide (120 atm) before addition of benzene the major products are cyclohexyl phenyl ketone and cyclohexenyl cyclohexyl ketones.

FORMYLATION reactions of aromatic compounds are known to occur using mixtures of carbon monoxide and hydrogen chloride in the presence of $AlCl_3$ and a small amount of Cu_2Cl_2, *i.e.* Gattermann–Koch conditions.[1-3] Other catalyst systems such as $HF–BF_3$ [4] and $HF–SbF_5$ [5] have also been investigated for this reaction, and more recently Olah *et al.*[6] have compared the reactivity and regioselectivity of the catalyst systems $CO–HF–SbF_5$, $HCOF–BF_3$, $CO–HCl–AlCl_3–Cu_2Cl_2$, $CO–HCl–AlCl_3$, and $CO–HF–BF_3$ for the formylation of an equimolar mixture of benzene and toluene. We have shown recently [7] that trifluoromethanesulphonic acid (triflic acid) is a very effective catalyst for the Koch carboxylation of alkenes especially at atmospheric pressure, where the high solubility of carbon monoxide in the acid is a critical factor. It was of interest to investigate whether this acid could also catalyse formylation and acylation reactions of aromatic compounds, and the results of this investigation are now reported.

Formylation reactions of arenes

Substrate	CF_3SO_3H : arene molar ratio	Pressure of CO (atm)	Time/h	Product (% yield)
C_6H_6	1 : 1	1	16	C_6H_5CHO (1)
	1.7 : 1	125	4	C_6H_5CHO (5)
C_6H_5Me	1 : 1	1	16	4-MeC_6H_4CHO (5)
	1.7 : 1	125	4	4-MeC_6H_4CHO (72)
1,4-$Me_2C_6H_4$	4.1 : 1	100	3	2,5-$Me_2C_6H_3CHO$ (41)
1,3-$Me_2C_6H_4$	6.8 : 1	100	3	2,4-$Me_2C_6H_3CHO$ (98)
$Pr^iC_6H_5$	6.8 : 1	100	3	4-$Pr^iC_6H_4CHO$ (32)
				1,4-$Pr^i{}_2C_6H_4$ (2)
				1,3,4-$Pr^i{}_3C_6H_3$ (7)
				2,5-$Pr^i{}_2C_6H_3CHO$ (31)
1,3,5-$Me_3C_6H_3$	1.7 : 1	1	18	2,4,6-$Me_3C_6H_2CHO$ (8)
	1.7 : 1	90	4	2,4,6-$Me_3C_6H_2CHO$ (35)
	1.7 : 1	90	10	2,4,6-$Me_3C_6H_2CHO$ (46)
	6.8 : 1	120	3	2,4,6-$Me_3C_6H_2CHO$ (98)

RESULTS AND DISCUSSION

When dry carbon monoxide was bubbled through a stirred, equimolar mixture of anhydrous triflic acid and benzene at room temperature for 16 h the product mixture contained only a trace (<1%) of benzaldehyde. Under similar conditions toluene gave only a 5% yield of 4-tolualdehyde, together with a small amount of a mixture of 2,6- and 2,7-dimethylanthracene. The latter did not arise by acid-catalysed condensation of two molecules of 4-tolualdehyde, since a mixture of the aldehyde and triflic acid at room temperature failed to give these products even after three weeks. This fact, and the knowledge that the same dimethylanthracene isomers have been detected among the products from other Friedel–Craft reactions of toluene,[8] make it probable that they are formed directly from toluene by generation of the benzyl carbocation. The atmospheric carbonylation of mesitylene (see Table) over 18 h at room temperature similarly gave only a poor yield (8%) of mesitylenecarbaldehyde. Under these conditions, using 1 atm of carbon monoxide, it would appear that despite the relatively high solubility of carbon monoxide in triflic acid, the CO concentration is a limiting factor in these formylation reactions.

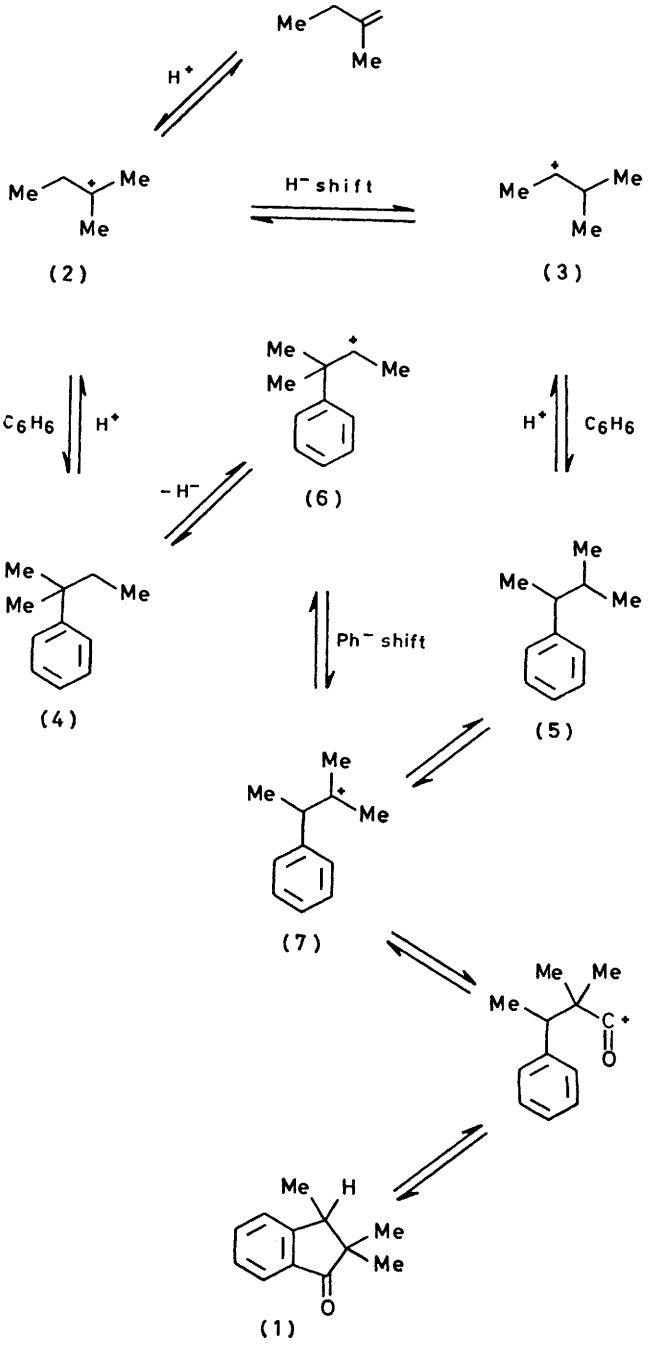
Greatly improved yields of the aromatic aldehydes were achieved when a mixture of triflic acid and the aromatic substrate was stirred under a CO pressure of 100—125 atm at room temperature during 3—4 h (see Table). Although the yield of benzaldehyde from benzene increased only to 5% under these conditions, by suitable choice of triflic acid : aromatic substrate ratio, CO pressure, and reaction time it proved possible to obtain an almost quantitative conversion of toluene and mesitylene to the corresponding aldehydes. It is interesting that the reactions of toluene gave only 4-tolualdehyde, with no evidence for any of the 2- or 3-isomers found on formylation with other superacid catalyst systems,[6] although a comparison of these different systems is probably not meaningful in view of the different temperatures and CO pressures employed. The

same regioselectivity was also obtained with *m*- and *p*-xylene which gave only 2,4- and 2,5-dimethylbenzaldehyde, respectively (see Table). There was no evidence for any products arising by isomerisation of either the hydrocarbon or the aldehyde, such as noted previously [9] in the formylation of *p*-xylene under Gattermann–Koch conditions.

The triflic acid-catalysed formylation of cumene was complicated by appreciable dissociation of the isopropyl substituent leading to 1,4-di-isopropylbenzene and 1,3,5-tri-isopropylbenzene. Benzene, which was probably also formed in this reaction, was not detected, but may have been lost during work-up. The major aldehyde products from this reaction were 4-isopropylbenzaldehyde and 2,5-di-isopropylbenzaldehyde. Formylation of anisole did not occur either at atmospheric or at high CO pressure, and the anisole was recovered almost quantitatively. This confirms other reports that phenols and phenol ethers can not be formylated under Gattermann–Koch conditions.[2,3]

Work in our laboratory has shown [10] that alkylation of aromatic compounds takes place using an alkene in the presence of triflic acid at room temperature giving high product yields. This suggested the possibility of combining the alkylation reaction with the formylation reaction as a method for the direct synthesis of aromatic aldehydes from benzene. Addition of a solution of cyclohexene in CCl_4 over a period of 1 h from a high-pressure syringe into a mixture of benzene and triflic acid (alkene : benzene : acid molar ratio, 1 : 4.7 : 8) under CO (100 atm) at room temperature, followed by stirring for 3 h, gave cyclohexylbenzene (33%) and 4-cyclohexylbenzaldehyde (34%) together with several minor, higher-boiling products. When this reaction was repeated with an alkene : benzene : acid molar ratio of 1 : 1 : 8, a CO pressure of 120 atm, and an extension to 60 h, there was no significant improvement in the yield of the aldehyde product. The structure of the aldehyde from these reactions was confirmed by preparation of an authentic sample in 41% yield by formylation of cyclohexylbenzene in triflic acid (molar ratio 1 : 7.1) at room temperature for 4 h under 120 atm of carbon monoxide. Addition of a solution of cyclopentene in CCl_4 to benzene–triflic acid under CO (115 atm) at room temperature gave cyclopentylbenzene (47%) and 4-cyclopentylbenzaldehyde (33%), together with smaller amounts of a tricyclopentylbenzene (5%) and a high-boiling aldehyde, possibly a dicyclopentylbenzaldehyde.

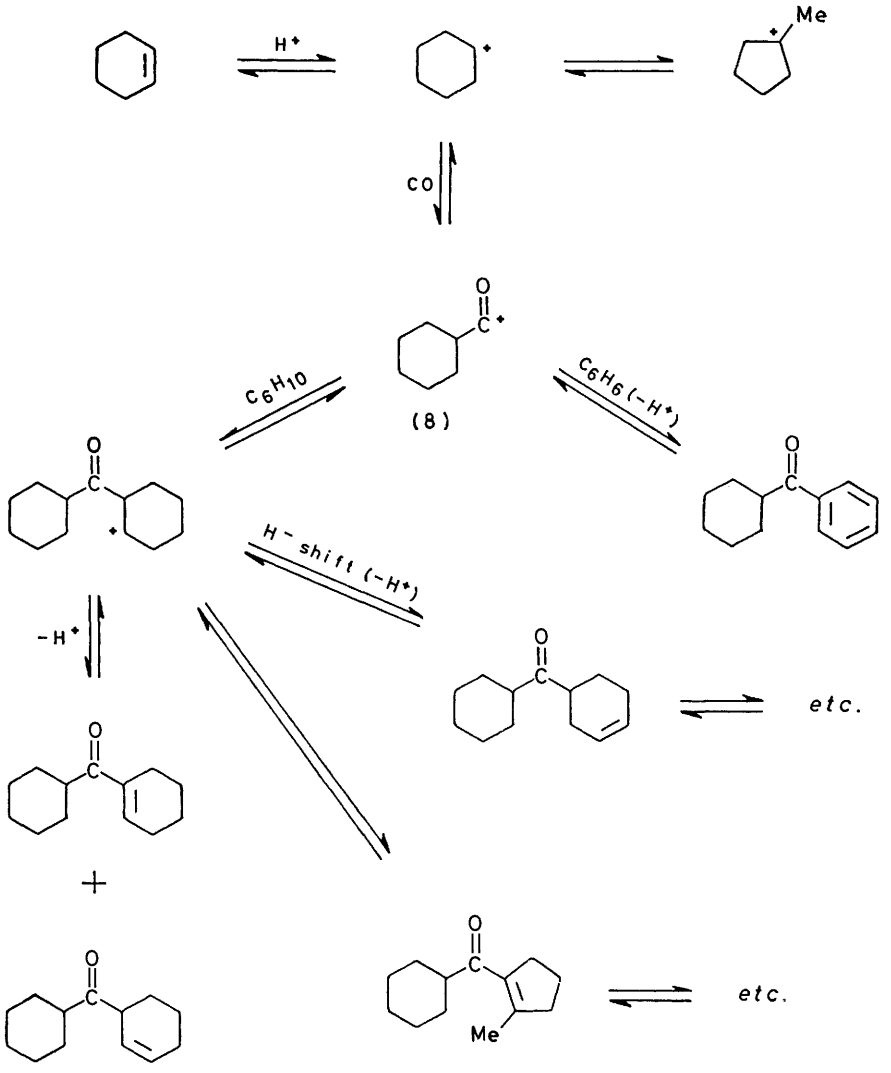
Attempts to extend this reaction to an acyclic alkene, 2-methylbut-1-ene, resulted in an interesting cyclization to form 2,2,3-trimethylindan-1-one (1) (38%) as one of the major products. Other products from this reaction included two alkenyl alkyl ketones (possibly $MeCH{=}CMeCH_2COCMe_2Et$ and $EtMeC{=}CHCOCMe_2Et$); a mixture of 2-methyl-3-phenylbutane and 2-methyl-2-phenylbutane; and several other unidentified compounds, but no aldehyde products. The trimethylindanone was fully characterised by i.r. spectroscopy, a lanthanide-shift analysis of its ^1H n.m.r. spectrum, and preparation of a 2,4-dinitrophenylhydrazone. The most rational explanation for its formation is by the reaction sequence shown in Scheme 1. The initially formed carbocation (2) is in equilibrium with the less stable carbocation (3),



SCHEME 1

leading to the alkylbenzene intermediates (4) and (5), respectively. Hydride-ion abstraction by ions (2) or (3), or by triflic acid, gives the tertiary carbocation (7), which forms the observed products by carbonylation and intramolecular cyclisation. Some support for this

mechanism comes from the observation that slow addition of 2-methylbut-1-ene to a mixture of 2-methyl-3-phenylbutane in anhydrous triflic acid (molar ratio 1 : 2.7) under a CO pressure of 120 atm gave, after stirring for 3 h at room temperature, 2,2,3-trimethylindan-1-one (21%). Other products of this reaction included 2,2-dimethylbutanoic acid, benzene, 2-methylbutane, 2-methyl-2-phenylbutane, a C_6H_{14} hydrocarbon, several polyalkylated benzene derivatives, and the same alkenyl alkyl ketones as were formed in the previous reaction. When 2-methylbut-1-ene was added to a mixture of anhydrous triflic acid and 2-methyl-2-phenylbutane (molar ratio 7.8 : 1) under similar conditions the products were 2,2,3-trimethylindan-1-one (39%); 2,2-dimethylbutanoic acid; C_5H_{12} and C_6H_{14} hydrocarbons; benzene; alkenyl alkyl ketones; a mixture of 2-methyl-3-phenylbutane and 2-methyl-2-phenylbutane; 10—15 unidentified minor products; and two high-boiling products, which from their mass spectra could be 2,2,3-trimethylindan-1-one derivatives having a pentyl substituent in the aromatic ring. From these results it is apparent that both pentylbenzene isomers are in equilibrium under the conditions of the reaction and give a very similar product mixture. The fact that benzene and polyalkylated products are also formed in these reactions suggests that isomerisation of (4) to (5) can occur by dealkylation to the cation (2), and hence the isomer (3), followed by re-alkylation. Isomerisation could also occur by hydride-ion abstraction from (4) or (5) giving the cations (6) and (7), respectively, followed by phenyl migration. Attempts to extend this intramolecular acylation reaction to 2-methyl-4-phenylpentane gave a small amount of 2,2-dimethylbutanoic acid, together with 2-methylbutane, a C_6H_{14} hydrocarbon, benzene, a compound thought to be 1,1,3-trimethylindane, and 18 other minor products which were not identified. From their i.r. spectra these appeared to be mainly hydrocarbon products rather than carbonyl compounds. The major products thus arise by dealkylation and isomerisation of the 2-methyl-4-phenylpentane. The formation



SCHEME 2

of 1,1,3-trimethylindane as one of the products indicates that the desired carbocation, $PhCMeCH_2\overset{+}{C}Me_2$ is formed, but the more favourable contact between the aromatic ring and the electrophilic centre favours intramolecular cyclisation rather than prior carbonylation to the acylium ion, as found with 2-methyl-3-phenylbutane.

By slight variation in the experimental procedure used for the formylation of benzene in the presence of cyclohexene, it is possible to change the major product from the formylation product, cyclohexylbenzaldehyde, to acylation products. So, for example, slow addition of cyclohexene to an eight-fold excess of anhydrous triflic acid under CO (100 atm), followed by addition of a three-fold excess of benzene, gave, after stirring for 3 h at room temperature, cyclohexyl phenyl ketone (44%) and three isomeric cyclohexenyl cyclohexyl ketones as the major products. The same three ketones, together with smaller amounts of another three isomers of these ketones, were obtained upon carbonylation of cyclohexene alone under similar conditions. One of these ketones was identified as cyclohex-1-en-1-yl cyclohexyl ketone by comparison with an authentic sample prepared in 40% yield by reaction of cyclohex-1-ene carbonyl chloride with cyclohexylmagnesium bromide. The other two major products are thought to be cyclohex-2-en-1-yl and cyclohex-3-en-1-yl cyclohexyl ketone, respectively. Under these conditions of high CO pressure there is little isomerisation of the initially formed cyclohexyl cation to methylcyclopentyl cation, in agreement with the results obtained for the Koch carbonylation reactions of cyclohexene catalysed by triflic acid.[7] The mechanistic steps leading to the observed products of these acylation reactions are outlined in Scheme 2. From this it can be appreciated that benzene and cyclohexene compete for the cyclohexyl acylium ion intermediate (8). It is possible that improved yields of alkyl aryl ketones could be achieved by slow addition of a mixture of the alkene and a large excess of the aromatic compound to triflic acid maintained under a high CO pressure, but this modification was not investigated. In these acylation reactions it is essential that the triflic acid used should be absolutely anhydrous, since even traces of water will result in the formation of carboxylation products.

EXPERIMENTAL

All aromatic starting materials were commercial samples purified by distillation and dried over sodium. The trifluoromethanesulphonic acid was purified by distillation and the fraction of b.p. 160—162 °C was used in these reactions. I.r. spectra were recorded on Perkin-Elmer spectrophotometers (models 137, 157 or 735), and ^1H n.m.r. spectra were recorded on Perkin-Elmer R10, R20, or R32 spectrometers. G.l.c. analyses were carried out using a Pye 104 gas chromatograph fitted with a flame-ionisation detector and 2-m SE 30 columns. For g.l.c.–m.s. analyses this was linked to an A.E.I. MS 902 mass spectrometer. In all the reactions described the trifluoromethanesulphonic acid was recovered from the product mixtures by precipitation as its barium salt, and regeneration by treatment with 100% sulphuric acid as described previously.[7]

General Procedure for the Formylation of Aromatic Substrates at Atmospheric Pressure.—A two-necked flask fitted with a magnetic stirrer, a gas inlet bleed, and a low-temperature (−78 °C) condenser, was charged with anhydrous triflic acid (15.0 g, 100 mmol), and dry CO was bubbled through the acid while stirring for 15 min. The dry aromatic compound (100 mmol) was then added, and the mixture was stirred for 16 h while passing carbon monoxide. After pouring the solution into ice–water, the organic layer was separated. The aqueous layer was washed several times with dichloromethane, and the washings were added to the organic layer. The combined organic phase was then washed with water and extracted with 2N KOH solution. Acidification of the alkaline extract often gave low yields of carboxylic acid products. Removal of the solvent and uncharged aromatic compounds from the organic phase gave a residue which was analysed quantitatively for aldehyde by g.l.c.

General Procedure for Formylation at High Pressures.—A stainless-steel autoclave (100-ml capacity), fitted with a 'Magnadrive' head, was charged with the desired quantities of anhydrous triflic acid and the dry aromatic substrate, and was then pressurised to 90—125 atm with carbon monoxide. After stirring for several hours if a pressure drop was observed, the autoclave was repressurised, and stirring was continued until there was no further pressure drop. After venting the carbon monoxide, the reaction mixture, which was usually deep red, was decomposed by pouring onto ice, and the same work-up procedure as described above was followed to isolate the products.

Details of the results are given in the Table. The products of the reactions of benzene, toluene, *m*- and *p*-xylenes, and mesitylene were analysed by g.l.c., and characterised by comparison of their i.r., ^1H n.m.r., and mass spectra with those of authentic samples. In the case of the cumene reaction the products were separated and analysed by g.l.c.–m.s., and yields were based on quantitative g.l.c. analysis.

The Formylation of Cyclohexylbenzene formed in situ *from Cyclohexene and Benzene.*—Anhydrous triflic acid (40.0 g, 266 mmol, 23.5 ml) and dry benzene (12.2 g, 156 mmol, 14.1 ml) were charged into a 100-ml stainless-steel autoclave which was then pressurised to 100 atm with carbon monoxide. The contents were stirred and a solution of cyclohexene (2.7 g, 33 mmol) in CCl_4 (28.5 ml) was injected into the autoclave from a high-pressure syringe during 1 h. Stirring was continued for a further 3 h before venting, pouring the contents onto ice, and work-up. A g.l.c.–m.s. analysis of the product mixture showed cyclohexylbenzene (33%), 4-cyclohexylbenzaldehyde (34%), and eight other minor components which could not be characterised. The presence of 4-cyclohexylbenzaldehyde was confirmed by preparation of its 2,4-dinitrophenylhydrazone, m.p. 230—233 °C (lit.,[11] m.p. 226—227 °C), followed by liberation of the pure aldehyde [δ_H (CCl_4) 1.2—2.0 (10 H, m, cyclohexyl CH_2), 2.5 (1 H, m, cyclohexyl-CH), 7.15 (2 H, d, A part of AA'XX' spectrum, J_{AX} 7.5 Hz), 7.55 (2 H, d, X component), 9.7 (1 H, s, CHO)] from the hydrazone by hydrolysis with a 15% w/v aqueous solution of $TiCl_3$ according to a reported procedure.[12]

When this reaction was repeated using anhydrous triflic acid (40.0 g, 266 mmol, 23.5 ml), benzene (2.6 g, 33 mmol, 3.0 ml), cyclohexene (2.7 g, 33 mmol) in CCl_4 (28.5 ml) and CO (120 atm) work-up after 60 h gave cyclohexanecarboxylic acid (0.35 g, 8%), cyclohexylbenzene (5%), 4-cyclohexylbenzaldehyde (31%), and higher-boiling products which

were probably polyalkylated benzenes and their formylated products; 34% of the benzene was recovered unchanged.

The Formylation of Cyclohexylbenzene.—Cyclohexylbenzene (25.9 g, 162 mmol, 81%), b.p. 235—236 °C (lit.,[13] 235—236 °C), was prepared by catalytic hydrogenation of biphenyl (30.8 g, 200 mmol) in glacial acetic acid (150 ml) according to a previously reported procedure.[14]

A mixture of cyclohexylbenzene (3.8 g, 23.8 mmol, 4 ml) and anhydrous triflic acid (25.5 g, 170 mmol, 15 ml) was charged into an autoclave which was then pressurised to 120 atm with CO, and the contents were stirred for 4 h before analysis of the product mixture by g.l.c., which showed benzene (25%) and 4-cyclohexylbenzaldehyde (41%), characterised as its 2,4-dinitrophenylhydrazone (m.p. 230—233 °C); 7% of the cyclohexylbenzene was recovered.

The Formylation of Cyclopentylbenzene formed in situ *from Cyclopentene and Benzene.*—Addition of a solution of cyclopentene (2.3 g, 33 mmol) in CCl_4 (28.5 ml) to a stirred solution of anhydrous triflic acid (40.0 g, 266 mmol, 23.5 ml) and dry benzene (12.2 g, 156 mmol, 14.1 ml) under 115 atm of CO, gave, after stirring for 3 h at room temperature, and analysis of the product mixture by g.l.c.–m.s., cyclopentylbenzene (47%), 4-cyclopentylbenzaldehyde (33%), tricyclopentylbenzene (5%), an unidentified aromatic hydrocarbon (*m/e* 168, 6%), and a high-boiling carbonyl compound (9%) which is possibly a dicyclopentylbenzaldehyde isomer. The percentages given represent percentage fractions based on g.l.c. peak areas. Treatment of the crude product mixture with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of 4-cyclopentylbenzaldehyde (m.p. 206—210 °C), from which the pure aldehyde [δ_H (CCl_4) 1.3—2.2 (8 H, m, cyclopentyl-CH_2), 2.6—3.3 (1 H, m, cyclopentyl-CH), 7.3 (2 H, d, A component of AA'XX' spectrum, J_{AX} 7.5 Hz), 7.7 (2 H, d, X component), and 9.85 (1 H, s, CHO)] was obtained by hydrolysis with aqueous $TiCl_3$ solution.

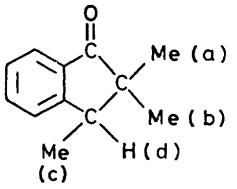
Reaction of 2-Methylbut-1-ene with Benzene.—2-Methylbut-1-ene (2.3 g, 33 mmol) in CCl_4 (28.5 ml) was injected from a high-pressure syringe during 1 h into a stirred solution of anhydrous triflic acid (40.0 g, 266 mmol, 23.5 ml) and dry benzene (12.2 g, 156 mmol, 14.1 ml) under CO (115 atm), and the mixture was stirred at room temperature for 3 h. Work-up and analysis of the product mixture by g.l.c.–m.s. gave alkenyl alkyl ketones (16%) thought to be a mixture of $EtMeC{=}CHCOCMe_2Et$ and $MeCH{=}CMeCH_2COCMe_2Et$; a mixture of 2-methyl-3-phenylbutane and 2-methyl-2-phenylbutane (21%); 2,2,3-trimethylindan-1-one (38%); and several other minor components which could not be identified. The percentages represent percentage fractions based on g.l.c. peak areas; where possible these were calibrated using authentic samples. The 2,2,3-trimethylindan-1-one (1a) was characterised by preparation of its 2,4-dinitrophenylhydrazone, m.p. 232—235 °C (lit.,[15] m.p. 243—244 °C), and by hydrolysis to the pure ketone, which was identified from its i.r. and mass spectra, and the ^1H n.m.r. spectrum [$\delta(CCl_4)$: 1.0 (s, H_a), 1.2 (s, H_b), 1.3 (d, H_c, J_{cd} 7.3 Hz), 3.0 (q, H_d), and 7.0—7.8 (m, aromatic) in the relative intensities of 3 : 3 : 3 : 1 : 4].

It was established beyond doubt that the product had structure (1a), rather than the isomeric structure (1b) by addition of successive increments of the lanthanide shift reagent $Eu(dpm)_3$, which indicated quite clearly that the $C(CH_3)_2$ group was adjacent to the carbonyl group.

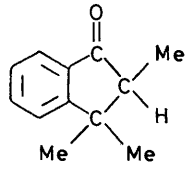
Carbonylation of 2-Methyl-3-phenylbutane.—2-Methyl-3-phenylbutane was prepared by catalytic hydrogenation (5% Pd–charcoal) of 3-methyl-2-phenylbut-2-ene, obtained by dehydration (anhydrous oxalic acid) of 3-methyl-2-phenylbutan-2-ol.[15]

A solution of 2-methylbut-1-ene (2.4 g, 34.2 mmol) in CCl_4 (28.5 ml) was added slowly over 1 h to anhydrous triflic acid (13.7 g, 91 mmol, 8.0 ml), 2-methyl-3-phenylbutane (5.0 g, 34.2 mmol), and CCl_4 (10 ml) under CO (120 atm), and the mixture was stirred at room temperature for 3 h. G.l.c.—m.s. analysis of the product mixture gave 2,2-dimethylbutanoic acid (4%),* isopentane and a C_6H_{14} hydrocarbon (11%); * benzene (12%); † alkenyl alkyl ketones (18%); * dialkylated benzenes (21%); * 2,2,3-trimethylindan-1-one (21%); † a mixture of 2-methyl-3-phenylbutane and 2-methyl-2-phenylbutane (35%); and six other unresolved components which were probably polyalkylated benzene derivatives.

Carbonylation of 2-Methyl-2-phenylbutane.—Addition of 2-methylbut-2-ene (4.8 g, 68.4 mmol) in CCl_4 (28.4 ml) during 1 h to a stirred solution of anhydrous triflic acid (40.0 g, 266 mmol, 23.5 ml) and 2-methyl-2-phenylbutane



(1a)



(1b)

(5.0 g, 34.2 mmol, 5.7 ml), under CO (115 atm), followed by stirring at room temperature for 3 h, gave a product mixture shown by g.l.c.—m.s. to contain isopentane and a C_6H_{14} hydrocarbon (7%); * benzene (15); † alkenyl alkyl ketones (9%); * a mixture of 2-methyl-3-phenylbutane and 2-methyl-2-phenylbutane (4%); † 2,2,3-trimethylindan-1-one (39%); † and 10—15 minor components which were not identified. A small amount (0.2 g, 2%) of 2,2-dimethylbutanoic acid was also isolated from this reaction.

Attempted Carbonylation of 2-Methyl-4-phenylpentane.—The 2-methyl-4-phenylpentane was synthesised by catalytic hydrogenation of 4-methyl-2-phenylpent-2-ene, obtained by dehydration (anhydrous oxalic acid) of 4-methyl-2-phenylpentan-2-ol, prepared from 4-methylpentan-2-one and phenylmagnesium bromide.

Addition of a solution of 2-methylbut-1-ene (4.8 g, 68.4 mmol) in CCl_4 (28.5 ml) over 1 h to anhydrous triflic acid (40.0 g, 2.66 mmol, 23.5 ml) and 2-methyl-4-phenylpentane (5.5 g, 34.2 mmol) under CO (105 atm), followed by stirring for 3 h at room temperature, gave 2,2-dimethylbutanoic acid (0.4 g, 3.4 mmol, 5%) and a neutral fraction shown by g.l.c.–m.s. to contain 2-methylbut-1-ene (10%); * a C_6H_{14} hydrocarbon (33%); ‡ benzene (29%); ‡ a series of 18 unresolved components, of which the major component (*ca.* 47% of total area) had a parent ion at *m/e* 158 and a base peak at *m/e* 143, and another component (parent ion *m/e* 160 and base peak *m/e* 159) thought to be 1,1,3-trimethylindane (*ca.* 27%).‡

Acylation of Benzene with the Products of Carbonylation of Cyclohexene.—A solution of cyclohexene (2.7 g, 33 mmol) in CCl_4 (28.5 ml) was injected over a period of 1 h by means of a high-pressure syringe into anhydrous triflic acid (40.0 g,

* Based on 2-methylbut-1-ene.
† Based on 2-methyl-3-phenylbutane.
‡ Based on 2-methyl-4-phenylpentane.

266 mmol, 23.5 ml) under CO (100 atm). The syringe was then depressurised, washed out with CCl_4, reloaded with benzene and repressurised to 100 atm with CO. The benzene (8.7 g, 112 mmol) was injected over 20 min into the autoclave which had been maintained throughout under a CO pressure of 100 atm. The mixture was stirred for several hours before working up in the usual manner to yield a carboxylic acid fraction (0.2 g, 5%) consisting mainly of cyclohexanecarboxylic acid with only a small amount of 1-methylcyclopentanecarboxylic acid. Analysis of the neutral products by g.l.c.–m.s. showed unreacted benzene (65% recovery); cyclohexylbenzene (6%); three isomeric cyclohexenyl cyclohexyl ketones (54%); and cyclohexyl phenyl ketone (40%) [all percentage yields are based on the cyclohexene taken]. The presence of cyclohexyl phenyl ketone was confirmed by preparation of its 2,4-dinitrophenylhydrazone, m.p. 187—189 °C (lit.,[13] m.p. 192 °C) [δ_H ($CDCl_3$) 1.1—1.9 (10 H, m, cyclohexyl-CH_2), 2.4 (1 H, m, cyclohexyl-CH), 7.0—7.1 and 7.3—7.4 (5 H, 2 × m, Ph), 7.8 (1 H, d, A component of ABX pattern, J_{AB} 10 Hz), 8.1 (1 H, dd, B component), and 8.8 (1 H, d, X component, J_{AX} 2 Hz); the NH signal was not detected].

Carbonylation of Cyclohexene.—Cyclohexene (2.7 g, 33 mmol) in CCl_4 (28.5 ml) was added during 1 h to anhydrous triflic acid (40.0 g, 266 mmol, 23.5 ml) under CO (100 atm), and the mixture was stirred for 1 h at room temperature to give a carboxylic acid fraction (1.7 g, 40%) containing mainly cyclohexanecarboxylic acid. The neutral products on analysis by g.l.c.—m.s. were found to contain six cycloalkenyl cycloalkyl ketones (*m/e* 192), of which the three major components, 15%, 26%, and 45%, respectively, had identical retention times to those obtained in the previous experiment. One of these components had an identical g.l.c. retention time and mass spectrum to those of an authentic sample of cyclohex-1-enyl cyclohexyl ketone,[16] prepared from cyclohex-1-en-1-carbonyl chloride [17] by reaction with cyclohexylmagnesium bromide.

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