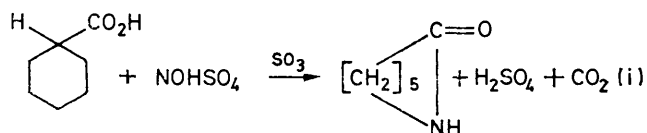


## Mixed Anhydrides of Cyclohexanecarboxylic Acid with Sulphonic Acids

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A new high-yield synthesis of mixed anhydrides of cyclohexanecarboxylic acid with sulphonic acids is described. The intramolecular thermal decomposition of these anhydrides when treated with solutions of nitrosylsulphuric acid in sulphuric acid may be assumed to proceed *via* pentamethyleneketene which has been recently postulated to be an intermediate in the SNIA Viscosa process for preparing  $\epsilon$ -caprolactam.

It has been postulated that the synthesis of  $\epsilon$ -caprolactam, which is the basis of the SNIA Viscosa process<sup>1</sup>



[equation (i)], involves pentamethyleneketene as an intermediate.<sup>2</sup> In *ca.* 88%  $\text{H}_2\text{SO}_4$ -12%  $\text{SO}_3$ , cyclohexanecarboxylic acid was thought by Deno *et al.*<sup>3</sup> to exist as a 1:1 mixture of the protonated carbonyl species and the acylium ion formed from this by dehydration. Acyl cations can be considered to be in equilibrium with ketenes. However, Maciel and Traficante,<sup>4</sup> who investigated the carbon-13 resonance of acetic and benzoic acid in sulphuric acid and oleum, produced evidence which was not consistent with Deno's findings. The nature of the species present in solutions of acetic acid in sulphuric acid and oleum has recently been reconsidered,<sup>5</sup> and the precursor to the acylium ion is assumed to be acetylsulphuric acid. Cyclohexanecarboxylic acid is known to react with oleum to give the mixed anhydride<sup>6</sup> which is rather unstable. In order to find direct evidence for the intermediacy of pentamethyleneketene in the synthesis

chlorides with sulphonic acids, and the second is less simple and consists of heating an excess of carboxylic anhydride with the sulphonic acid. We have developed a satisfactory method by which mixed anhydrides of cyclohexanecarboxylic acid can be prepared in excellent yields starting from equimolar amounts of sulphonic acids and pentamethyleneketene. We are not aware of any reports concerning addition of sulphonic acids to ketenes except Olah's communication<sup>8</sup> which briefly refers to the preparation of acetyl methanesulphonate from methanesulphonic acid and ketene. The low yields reported probably arise because ketene interacts with sulphur dioxide.<sup>9</sup> In our method, low temperatures are usually required in order to avoid dimerisation of pentamethyleneketene. After completing the addition of the sulphonic acid to the yellow pentamethyleneketene solution, the mixture is clear and colourless; removal of solvent at reduced temperature and pressure readily yields the mixed anhydride. The same anhydrides reported below may be prepared *via* cyclohexanecarbonyl chloride or cyclohexanecarboxylic anhydride.

The acylating properties of mixed sulphonic-carboxylic anhydrides are known. Indeed, on reaction with 2-naphthol, only acylated products were obtained; considering the powerful electron-withdrawing nature of the sulphonate group, the reaction may be assumed to

### Mixed anhydrides of cyclohexanecarboxylic acid with sulphonic acids; synthesis and acylating properties

Acid	Product	Solvent	Required (%) [Found (%)]		N.m.r. <sup>a</sup> ( $\delta$ )		2-Naphthol ester Yield (%) <sup>b</sup>
			C	H	S		
$\text{MeSO}_3\text{H}$	$\text{MeSO}_2\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{11}$	$\text{CHCl}_3$	46.5 [46.6]	6.8 [6.9]	15.5 [15.4]	2.46 (1H, m), 3.21 (3H, s)	98
$\text{PhSO}_3\text{H}$	$\text{PhSO}_2\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{11}$	$\text{CHCl}_3$	58.1 [58.2]	6.0 [6.0]	11.9 [11.8]	2.34 (1H, m), 7.54 (5H, m)	91
$p\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$	$p\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_{11}$	$\text{Et}_2\text{O}$	59.5 [59.4]	6.4 [6.5]	11.3 [11.2]	2.38 (3H, s), 7.60 (4H, q)	89
(1)	(2)	$\text{CH}_3\text{CN}$	52.8 [52.9]	6.9 [7.0]	10.0 [10.0]	2.52 (1H, m), 12.27 (1H, s)	94

<sup>a</sup> The resonances due to the remaining cyclohexane protons are not reported. <sup>b</sup> The loss of 2-naphthol may be followed by observing the absorption at 3300 Å; at this wavelength 2-naphthol has a moderately intense u.v. absorption band which is largely absent from the spectrum of its cyclohexanecarboxylate.

mentioned above, we have investigated mixed anhydrides of cyclohexanecarboxylic acid with sulphonic and sulphuric acids.

Few systematic investigations have been performed on the synthesis and properties of mixed sulphonic-carboxylic anhydrides. Two syntheses have recently been reported;<sup>7</sup> the first consists of treating acid

<sup>1</sup> I. Donati, G. Sioli, and M. Taverna, *Chimica e Industria*, 1968, **50**, 997.

<sup>2</sup> L. Giuffrè, E. Tempesti, G. Sioli, M. Fornaroli, and G. Airoidi, *Chem. and Ind.*, 1971, 1098.

<sup>3</sup> N. C. Deno, C. U. Pittman, jun., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, 1964, **86**, 4370.

<sup>4</sup> D. D. Traficante and G. E. Maciel, *J. Phys. Chem.*, 1966, **70**, 1314.

be displaced toward the  $\text{S}_{\text{N}}1$  end of the mechanistic spectrum even if alternative pathways such as a bimolecular synchronous displacement at the  $sp^2$ -hybridised carbon atom can be envisaged.<sup>10</sup> However, the mixed anhydride of cyclohexanecarboxylic acid with sulphuric acid was relatively stable. The formation of sulphaacetic acid from mixtures of sulphuric acid and

<sup>5</sup> A. Casadevall, A. Commeyras, P. Paillous, and H. Collet, *Bull. Soc. chim. France*, 1970, 719.

<sup>6</sup> L. Giuffrè, G. Sioli, and E. Losio, *Chimica e Industria*, 1969, **51**, 245.

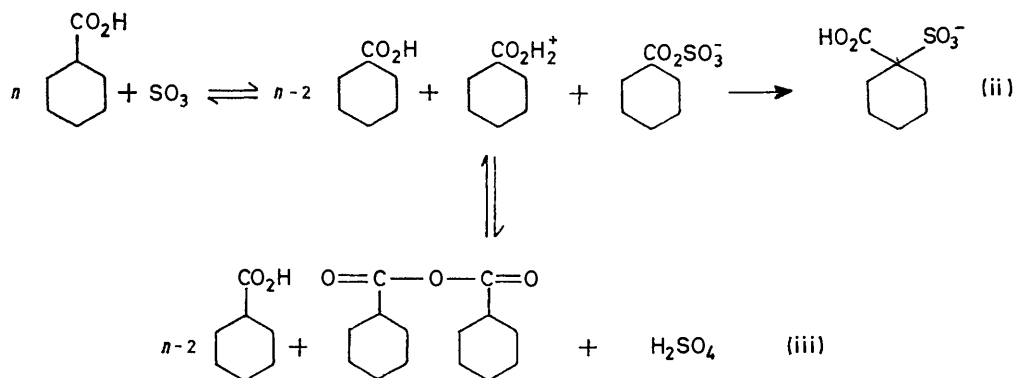
<sup>7</sup> M. H. Karger and Y. Mazur, *J. Org. Chem.*, 1971, **36**, 528.

<sup>8</sup> G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, 1962, **27**, 2667.

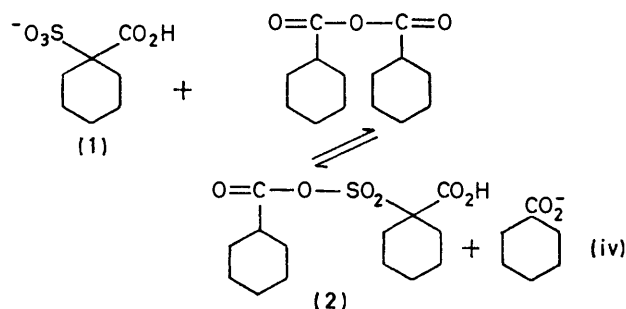
<sup>9</sup> A. Gomes and M. M. Jouillié, *Chem. Comm.*, 1967, 935.

<sup>10</sup> S. L. Johnson, *Adv. Phys. Org. Chem.*, 1967, **5**, 237.

acetic anhydride is well known and was recently confirmed to proceed *via* acetylsulphuric acid,<sup>11</sup> and accordingly, starting from cyclohexanecarboxylic acid and sulphur trioxide or cyclohexanecarboxylic anhydride and 100% H<sub>2</sub>SO<sub>4</sub>, the observation of gradual disappearance of sulphate ions indicated rearrangement of the mixed anhydride to  $\alpha$ -sulphocyclohexanecarboxylic acid [equations (ii) and (iii)].



The mixed anhydride of cyclohexanecarboxylic acid with sulphuric acid was found to be a sulphonating rather than an acylating agent. To avoid the rapid loss of sulphuric acid by sulphonation of the hydroxylic substrate, which would occur with the reactive 2-naphthol, we treated anisole with the mixed anhydride. Concurrent acylation occurred only if an excess of



anhydride over sulphuric acid was adopted. Thus the reaction was thought to proceed *via* an initial equilibrium between the carboxylic anhydride and the sulphocarboxylic acid gradually formed, to yield the mixed anhydride as the effective acylating agent [equation (iv)]. The correctness of this suggested mechanism was indicated experimentally and independently confirmed by reaction of pentamethyleneketen and  $\alpha$ -sulphocyclohexanecarboxylic acid.

Under the conditions currently used,<sup>12</sup> with a cyclohexanecarboxylic acid:oleum ratio greater than one, the pre-mixing phase of the SNIA Viscosa process may be reasonably assumed to involve rapid equilibria (ii)–(iv) between predominantly interconvertible species. If acyl cations may be considered as a resonance hybrid

of the oxonium, oxocarbenium, and keten-like forms,<sup>13</sup> then considering equilibrium (iv), acid-catalysed cleavage of the mixed anhydride to the corresponding cycloalkyl-oxocarbenium ion may lead to pentamethyleneketen under non-equilibrium conditions. The consistency of this assumption has been demonstrated. It has recently been reported<sup>7,14</sup> that thermal decomposition of acetyl methanesulphonate or its treatment with tertiary amines

yields keten and regenerates the sulphonic acid or its amine sulphonate salt respectively. Accordingly, we studied the thermal stability of the mixed anhydrides described above; the results are similar to those previously cited. Flash thermolysis of the mixed anhydrides gave pentamethyleneketen which was trapped and characterised by g.l.c. analysis. The yields were moderate (25–42%) and no attempts were made to optimise them. In addition, the high reactivity of these anhydrides led us to investigate their intramolecular decomposition when treated with sulphuric acid solutions of nitrosylsulphuric acid. Thus, starting from equimolar mixtures of  $\alpha$ -sulphocyclohexanecarboxylic acid and cyclohexanecarboxylic anhydride in carbon tetrachloride, after completing the addition at room temperature of the aqueous sulphuric acid solution of nitrosylsulphuric acid, heating to 75° caused evolution of carbon dioxide. After 25 min, the reaction was quenched; usual work-up gave  $\epsilon$ -caprolactam (66% based on NO<sup>+</sup>). Better yields were obtained starting from cyclohexanecarbonyl methanesulphonate.

#### EXPERIMENTAL

N.m.r. spectra were recorded with a Varian HA 100 spectrometer for 0.4M-solutions with [<sup>2</sup>H]chloroform as solvent and tetramethylsilane as internal reference. G.l.c. analyses were performed on a Carlo Erba model GT 200 gas chromatograph, using helium as carrier gas. U.v. measurements were made with a Gilford model 240 spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer 457 instrument.

*Reagents and Analyses.*—Pentamethyleneketen (98.8% pure by gas chromatography<sup>15</sup>) was prepared by pyrolysis

<sup>13</sup> G. A. Olah, *Angew. Chem. Internat. Edn.*, 1973, **12**, 173.

<sup>14</sup> M. H. Karger and Y. Mazur, *J. Org. Chem.*, 1971, **36**, 532.

<sup>15</sup> V. Giacobini and G. Lemetre, *Chimica e Industria*, 1972, **54**, 417.

<sup>11</sup> A. Casadevall and A. Commeyras, *Bull. Soc. chim. France*, 1970, 1850.

<sup>12</sup> L. Giuffrè and G. Sioli, *Chimica e Industria*, 1969, **51**, 787.

of twice distilled cyclohexanecarboxylic anhydride (SNIA Viscosa) according to Sioli *et al.*<sup>16</sup> The purity and water of hydration content for methanesulphonic, benzenesulphonic (Fluka), toluene-*p*-sulphonic (Merck), and  $\alpha$ -sulphocyclohexanecarboxylic acid<sup>17</sup> were established by a combination of aqueous and nonaqueous potentiometric titrations with standard basic titrants and Karl Fisher titrations.<sup>18</sup> 2-Naphthol and anisole were Carlo Erba reagent grade. The purity of 100% H<sub>2</sub>SO<sub>4</sub>, prepared by distilling sulphur trioxide into 98% H<sub>2</sub>SO<sub>4</sub> (Carlo Erba), has been conveniently assayed by measuring its specific conductance.<sup>19</sup> The composition of sulphuric acid solutions of nitrosylsulphuric acid (SNIA Viscosa; approximate weight composition: NOHSO<sub>4</sub> 72%, H<sub>2</sub>SO<sub>4</sub> 25%, SO<sub>3</sub> 3%) were adjusted with aqueous sulphuric acid solutions and analysed by conductometric and potentiographic techniques.<sup>20</sup> All solvents were rigorously purified prior to use by standard techniques.

*Mixed Anhydrides of Cyclohexanecarboxylic Acid with Sulphonic Acids.*—The experimental procedures for the mixed anhydrides described are similar to those reported below.

(a) *Cyclohexanecarbonyl methanesulphonate.* Pentamethyleneketone (5.51 g, 50.0 mmol) was dissolved in CHCl<sub>3</sub> (50 ml) at -20°; after completing the addition of methanesulphonic acid (4.80 g, 50.0 mmol), the mixture was stirred at 0° for 30 min. Solvent removal (0.1 mmHg; 10°) readily yielded the mixed anhydride (10.16 g, 98.5%). Traces of free acid (*ca.* 1%) were indicated in the n.m.r. spectrum. On attempted distillation, extensive decomposition occurred.

(b) *Reaction of cyclohexanecarbonyl methanesulphonate with 2-naphthol.* To a solution of cyclohexanecarbonyl methanesulphonate (10.51 g, 50.9 mmol) in CHCl<sub>3</sub> (100 ml) was added 2-naphthol (7.34 g, 50.9 mmol). The mixture was kept at room temperature. Samples were withdrawn at regular intervals and the 2-naphthol concentration was determined spectrophotometrically by measurements at 3300 Å. After 30 min, the solution was carefully neutralised with 5% sodium hydroxide solution and repeatedly extracted with ether to yield 2-naphthyl cyclohexanecarboxylate (12.68 g, 98%) whose spectral characteristics were identical with those of an authentic sample.<sup>21</sup>

(c) *Thermal decomposition of cyclohexanecarbonyl methanesulphonate.* Flash thermolysis (1.0 mmHg; 80°) of a solution of cyclohexanecarbonyl methanesulphonate (9.24 g, 44.7 mmol) in CHCl<sub>3</sub> (50 ml) caused decomposition as evidenced by evolution of gas and immediate darkening of the solution which left a brown residue on evaporation. The effluent gas was passed into dry ethanol cooled below

-40°; the collected pentamethyleneketone was characterised by g.l.c. analysis (42% yield). The residue was distilled under reduced pressure, the only product isolated in the distillate being methanesulphonic acid (3.09 g, 72%).

(d) *Nitrosodecarboxylation of cyclohexanecarbonyl methanesulphonate.* Addition of an aqueous sulphuric acid solution of nitrosylsulphuric acid (9.06 g; 4.67 mmol NO<sup>+</sup> g<sup>-1</sup>, 3.52 mmol H<sub>3</sub>O<sup>+</sup> g<sup>-1</sup>, 8.19 mmol HSO<sub>4</sub><sup>-</sup> g<sup>-1</sup>) to a clear solution of cyclohexanecarbonyl methanesulphonate (15.30 g, 74.19 mmol) in CCl<sub>4</sub> (80 ml) was performed at room temperature. On heating the mixture to 75° under vigorous stirring, carbon dioxide was evolved. After 10 min at 75° the mixture was quenched, adjusted to pH 8 with 20% sodium hydroxide solution, and repeatedly extracted with CHCl<sub>3</sub> to yield  $\epsilon$ -caprolactam (3.87 g, 81% yield).<sup>22</sup> The alkaline aqueous solution was acidified with dilute sulphuric acid and extracted with ether to yield cyclohexanecarboxylic acid (4.11 g; 96% pure by g.l.c. analysis).

*Mixed Anhydride of Cyclohexanecarboxylic Acid with Sulphuric Acid.*—(a)  *$\alpha$ -Sulphonation.* A solution of cyclohexanecarboxylic anhydride (9.96 g, 41.8 mmol) in CCl<sub>4</sub> (50 ml) was warmed to 50° and treated with 100% H<sub>2</sub>SO<sub>4</sub> (4.10 g, 41.8 mmol). The mixture was kept at 50° for 4 h after which time water (50 ml) was added and stirring was continued for 15 min. Usual work-up gave  $\alpha$ -sulphocyclohexanecarboxylic acid (2.66 g, 30.5% yield). Analytical results expressed in terms of sulphuric acid are not reliable since they include the sulphate of the unrearranged mixed anhydride which on hydrolytic desulphonation yields cyclohexanecarboxylic acid.

(b) *Reaction with anisole.* A mixture of cyclohexanecarboxylic anhydride (11.94 g, 50.1 mmol) and anisole (5.42 g, 50.1 mmol) in CCl<sub>4</sub> (70 ml) was warmed to 50° and treated with 100% H<sub>2</sub>SO<sub>4</sub> (4.91 g, 50.1 mmol). The mixture was kept at 50° for 15 min and then water (50 ml) was added and stirring was continued for 15 min. The separated aqueous layer was repeatedly extracted with ether and neutralised with 10% sodium hydroxide solution. The total yield of *p*-methoxybenzenesulphonic acid, whose sodium salt absorbs at 2310 Å, was 76%.

Under the same conditions, starting from cyclohexanecarboxylic anhydride (22.66 g, 95.0 mmol), anisole (7.71 g, 71.3 mmol), and 100% H<sub>2</sub>SO<sub>4</sub> (4.66 g, 47.5 mmol), usual work-up afforded *p*-methoxybenzenesulphonic acid (7.52 g, 39.9 mmol) and cyclohexyl *p*-methoxyphenyl ketone (3.43 g, 15.7 mmol) whose spectral characteristics were identical with those of an authentic sample.<sup>23</sup>

[3/1445 Received, 10th July, 1973]

<sup>16</sup> G. Sioli, R. Mattone, L. Giuffrè, R. Trotta, and E. Tempesti, *Chimica e Industria*, 1971, **53**, 133.

<sup>17</sup> E. Tempesti, L. Giuffrè, M. Fornaroli, and G. Airoldi, *Chem. and Ind.*, 1973, 183.

<sup>18</sup> D. J. Pietrzyk and J. Belisle, *Analyt. Chem.*, 1966, **38**, 969.

<sup>19</sup> W. H. Lee in 'The Chemistry of Non-aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York and London, 1967, vol. II, p. 99.

<sup>20</sup> L. Giuffrè and E. Losio, *Chimica e Industria*, 1968, **50**, 344; L. Giuffrè, E. Losio, and A. Castoldi, *ibid.*, 1966, **48**, 958.

<sup>21</sup> S. S. Bhargava, S. K. Jain, and G. S. Saharia, *Indian J. Chem.*, 1967, **5**, 543.

<sup>22</sup> L. Giuffrè and E. Santacesaria, *Chimica e Industria*, 1969, **51**, 1341.

<sup>23</sup> Y. Ogata, Y. Furuya, and M. Ito, *J. Amer. Chem. Soc.*, 1963, **85**, 3649.