The reaction between ethanedioyl (oxalyl) dihalides and $Ag_2C_2O_4$: a route to Staudinger's elusive ethanedioic (oxalic) acid anhydride

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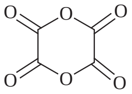
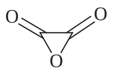
Ethanedioic (oxalic) acid anhydride 1 was prepared for the first time and its dimeric cyclic nature established by spectroscopic and chemical evidence. The strong instability of 2-chloro-2-oxoethanoic acid 3 was incidentally observed. The chemical behaviour of 1 with MeOH and CH_2N_2 was investigated.

Introduction

Well known low molecular weight carbon oxides are CO, CO_2 and C_3O_2,[1] the latter being a less stable substance. Oligomeric mixed oxides from CO and CO_2,[2] like **1** (C_4O_6) and **2** (C_2O_3), are not known and expected to be extremely unstable. Compounds **1** and **2** may be regarded as the so far unknown ethanedioic (oxalic) acid anhydrides, in the dimeric and monomeric form, respectively. The beginnings of an attempt at constructing **1** are to be found in a work by Staudinger,[3] who, in a passing remark, besides assessing the proven instability of 2-chloro-2-oxoethanoic acid (oxalic acid monochloride, **3**), also dealt with the likelihood of the intermediacy of **2** in the decomposition process. His efforts at observing any such products were unsuccessful, possibly because the experimental conditions were not suitable for their formation or persistence.

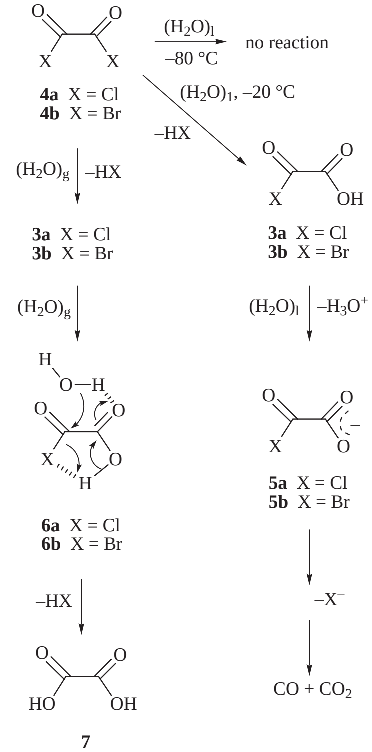


1

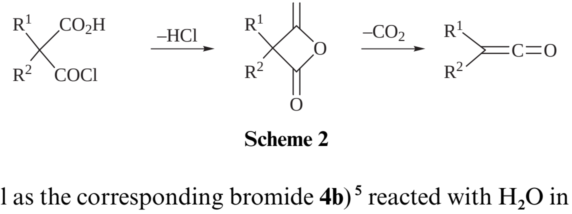


2

The theoretical evaluation by more and more sophisticated calculations of the enthalpies of formation, both from the atomized elements and from CO and CO_2, gave decreasing values for **1** and **2**.[4] As a consequence, cyclic co-oligomers of carbon monoxide and dioxide, made by a convenient route in an inert environment, might be stable enough not to find a monomolecular self-decomposition route, although free energy considerations are grossly in favour of such a process. In fact, initial breakdown of the putative molecules may be envisaged as: a) a one step concerted collapse into the monomeric species; b) a process initiated by the homolytic cleavage of a bond, followed by sequential loss(es) of monomeric units; c) a process similar to the one just mentioned, but involving an initial heterolytic cleavage producing a zwitterion. With these considerations in mind, we set out to carry out some pertinent investigations.



Scheme 1



Scheme 2

Results and discussion

Staudinger dealt with this topic in his experiments with $(COCl)_2$ **4a**[3] when he observed that this compound was decomposed by H_2O quantitatively to HCl, CO and CO_2, likely by the intermediacy of the anion **5a** of the monochloride **3a**, whereas $(COOH)_2$ **7** was not formed in the condensed phase (liquid H_2O) reaction (Scheme 1). On the other hand, the gas phase reaction between **4a** and H_2O led to **7**, perhaps through a hydrogen bonded H_2O molecule associated with the intermediate **3a** to give **6a**. In an analogous fashion, H_2S produced CO and COS. The intermediacy of the internal ethanedioic anhydride **2** was advanced by analogy with the reaction of the monochlorides of propanedioic acids en route to yielding diphenylketenes and CO_2, a process which occurs at a much slower rate (Scheme 2). Following the observation that **4a** (as well as the corresponding bromide **4b**)[5] reacted with H_2O in the *condensed* phase only to yield CO, CO_2 and HCl (or HBr), Staudinger eventually studied the reaction between **4a** and $Ag_2C_2O_4$ **8** in Et_2O, in order to obtain the dimeric anhydride **1**,

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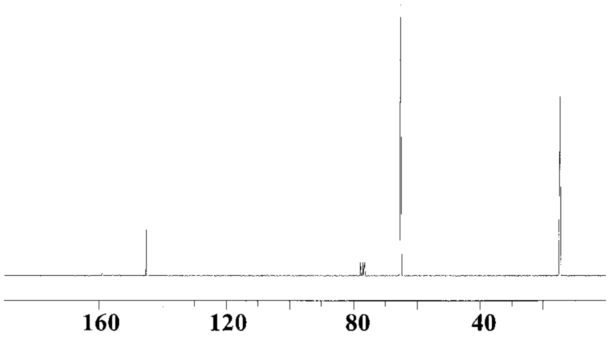
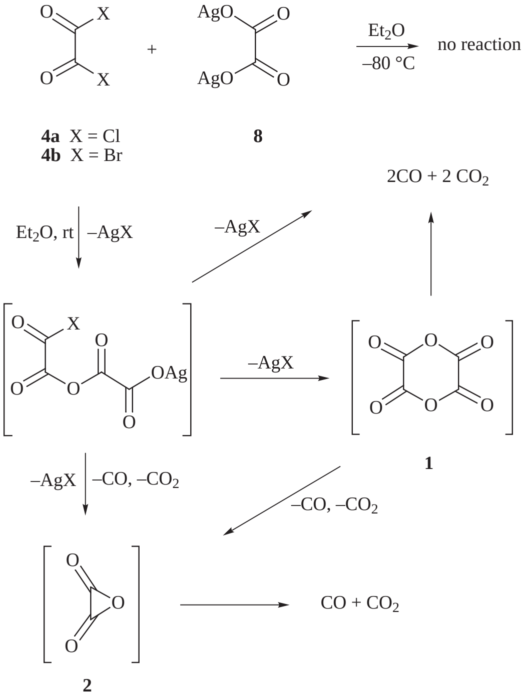


Fig. 1 ^{13}C NMR spectrum of **1**

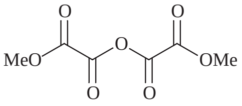
but, again, only CO and CO_2 were the products of the reaction.[3] He found that the reaction produced CO and CO_2 in an unspecified ratio at room temperature, but deduced that no reaction occurred at lower temperature, because there was no gas evolution. The assumed direct precursor of the evolved gases was the internal three membered ring oxalic anhydride **2**; alternative mechanisms are shown in Scheme 3.



Scheme 3

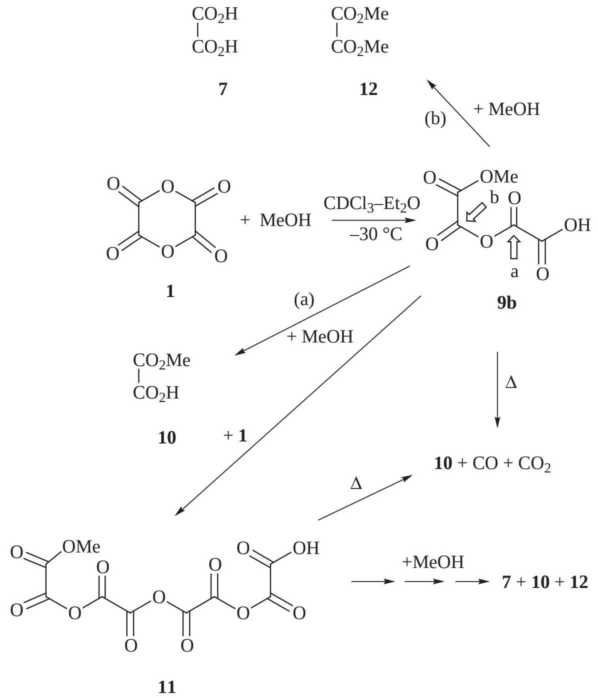
We repeated the latter reaction using Et_2O as solvent at *ca.* −15 °C, adding ethanedioyl dichloride **4** to a well stirred slurry of *ca.* 1.5 equivalents of $Ag_2C_2O_4$ **8**. After 1 h, filtration of the slurry, followed by evaporation of the volatile materials at reduced pressure and at a suitably low temperature, and eventual dissolution of the residue into a mixture of $CDCl_3$–Et_2O, gave a solution amenable to ^{13}C NMR analysis (Fig. 1). The obtained low temperature (−30 °C) spectrum was characterized by a sharp single peak at 144.94 ppm. The outcome of the reaction either with **4a** or the corresponding dibromide **4b** in Et_2O was identical. Allowing the solution, which seemed indefinitively stable at −30 °C, to warm up to close to 0 °C caused gas evolution to be observed, consisting of CO and CO_2 produced in a 1 : 1 ratio. The only interpretation plausible for the NMR observation is the formation of **1**, the observed value for the appearance of the new single peak being in good agreement with expectation (154 ppm).[6] By and large, during the decomposition of the newly formed product **1**, no further NMR peaks, aside from those for CO and CO_2, could be observed, thus ruling out the observable intermediacy of **2**, for which the predicted ^{13}C resonance value is 167 ppm.[6] This was the first evidence collected for the dimeric nature of the anhydride **1**.

We have subsequently observed the behaviour of the system ethanedioyl dichloride (**4a**)–H_2O, of which a possible reaction pathway[3] is the production of **3a** and **2** (Scheme 1). A suitable amount of H_2O (1 : 1 molar ratio) was added in one portion, either to a $CDCl_3$ or CD_3CN solution of **4a** at −30 °C and the reaction monitored by ^{13}C NMR spectroscopy. Besides decomposition of **4a**, the sole reaction products observed were CO and CO_2, generated in a relatively slow process, which can be rationalized in terms of an initial slow hydrolysis of the first COCl function to give **3a**, which very quickly proceeds to the final outcome by either of the two pathways outlined in Scheme 1, a result in agreement with Staudinger's report.[3]



9a

The anhydride **9a** of the monomethyl ester of ethanedioic acid (**10**) was found to be highly reactive with H_2O and alcohols.[7] As we can expect an enhanced reactivity of **1** towards nucleophilic substrates, we studied the behaviour of the cyclic anhydride with MeOH and CH_2N_2, respectively. Stepwise addition of dry MeOH at −30 °C to a $CDCl_3$–Et_2O solution of **1** allowed us to observe the initial consumption of the starting material with simultaneous formation of two products, *i.e.* the mixed anhydride **9b** of compound **10** with ethanedioic acid (**7**), accompanied by minor amounts of the supposed tetramer **11**, resulting from the addition of **9b** to a molecule of **1** according to Scheme 4, as hinted at by the recorded ^{1}H and ^{13}C NMR spectra (Figs. 2 and 3). Upon further addition of MeOH, the complete disappearance of **1** was observed, together with a decrease of compounds **9b** and **11** and the appearence of peaks for acids **7**, **10** and the dimethyl ester of ethanedioic acid (**12**). Finally, when excess MeOH was added, products **7**, **10** and **12** were the only ones found. The latter two compounds were present in the ratio 6 : 4, pointing to a possible unequivalence



Scheme 4

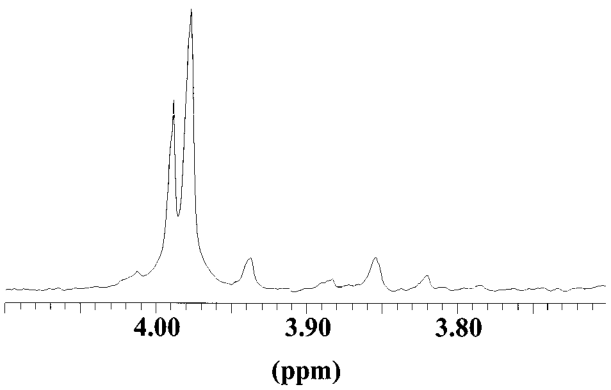


Fig. 2 ^1H NMR spectrum of the reaction mixture **1**–MeOH

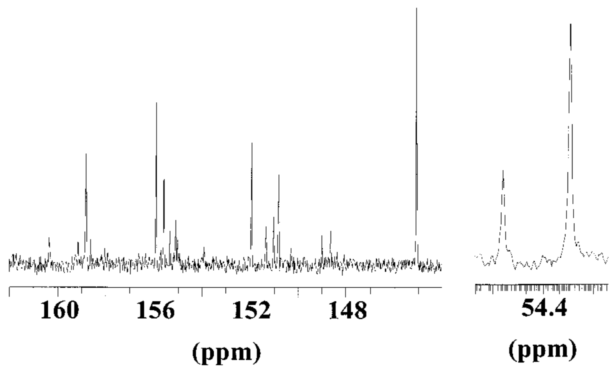
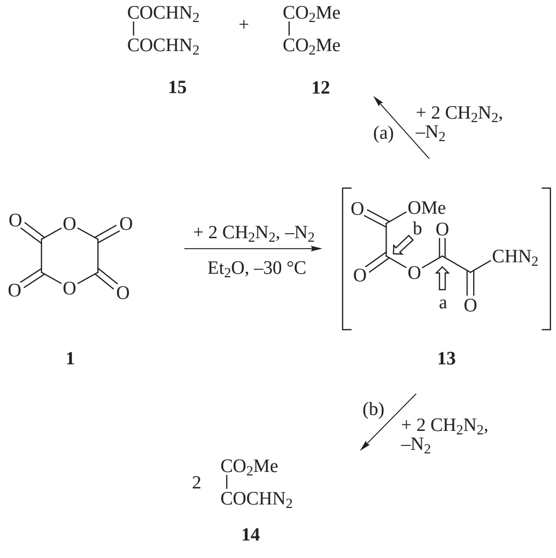


Fig. 3 ^{13}C NMR spectrum of the reaction mixture **1**–MeOH

of the two sites for attack of MeOH on the intermediate **9b**, as depicted in Scheme 4. In fact, for shorter reaction times the production of **10** and **12** appeared to be practically equally efficient, thus indicating a prevalence of pathway (b) over (a). Compounds **9b** and **11** looked relatively stable under the reaction conditions, though they underwent complete decomposition on standing at room temperature to yield CO, CO_2 and **10**.

Reaction of **1** with excess CH_2N_2 in dry Et_2O took two routes (Scheme 5), as clearly evinced by ^1H and ^{13}C NMR monitoring:



Scheme 5

most likely through the intermediacy of **13**. The prevalent route (b) yielded the diazoester **14**, whereas route (a) gave equimolar amounts of **12** and 1,4-bis(diazo)butane-2,3-dione (**15**), the ratio of **14**:**15** being 7:3. These results provided further structural evidence confirming the dimeric cyclic nature of the anhydride **1**.

Conclusion

The elusive mixed oligomer between CO and CO_2, represented by the cyclic anhydride **1**, whose synthesis and characterization is now achieved for the first time, adds a new entry to the small family of carbon oxides. The present simple access to **1** also yields the structural key to the actual anhydride of ethanedioic acid.

Experimental[8]

General methods

Unless otherwise specified, reagents and solvents were commercially available (Aldrich Italia, Milano, Italy) and used as received. The other reagents employed were prepared by conventional methods (see below). Ethanedioyl halides were carefully distilled prior to use and Et_2O was obtained anhydrous by freshly distilling it from sodium–benzophenone ketyl. Elemental analyses were obtained for all isolated compounds and were satisfactory. Unless otherwise indicated, NMR spectra were recorded in $CDCl_3$ or in $CDCl_3$–Et_2O 2:1 (v/v). Proton chemical shifts are reported in ppm on the δ scale relative to TMS (0.00) or, alternatively, to the center line of the Et_2O triplet (1.20) as an internal reference; the carbon chemical shifts are reported in ppm relative to the center line of the $CDCl_3$ triplet (77.00). GC–MS headspace analyses (isotherm 25 °C, He flow: 1 ml min^{-1}) were carried out using a 0.25 mm i.d. × 30 m CARBOXEN 1006 PLOT fused silica capillary column (Supelchem, Milano, Italy). $Ag_2C_2O_4$ (**8**)[9] was prepared in nearly quantitative yield by adding dropwise, at room temp. under stirring, an aqueous solution of $AgNO_3$ (60 mmol in 6 ml) into an aqueous solution of $Na_2C_2O_4$ (30 mmol in 140 ml); the white precipitate that formed was filtered, washed with a little EtOH, Et_2O, collected and dried at 40 °C under reduced pressure over P_2O_5 in the dark. The following compounds were obtained essentially according to described procedures.

Ethanedioic acid monomethyl ester (monomethyl oxalate, 10)[10]

Solid $(CO_2Me)_2$ (**12**, 50 mmol) was added in one portion under stirring to a solution of $KHCO_3$ (55 mmol) in H_2O (20 ml). After heating at 80 °C, the mixture became homogeneous and gas evolution was observed. The solution was stirred at the same temperature during 4 h, cooled to room temp., washed with Et_2O (2 × 15 ml), acidified with 37% aqueous HCl (6 ml), saturated with Na_2SO_4 and extracted with Et_2O (3 × 20 ml). The combined organic phase was dried over Na_2SO_4, concentrated to dryness and the obtained oily residue fractionally distilled, to give compound **10** (40% yield) as a colourless liquid which solidified on cooling; bp 49 °C/25 Pa;[11] ν_{max}(neat, melted)/cm^{-1} 3466s (br), 1752s, 1628w, 1448w, 1226s, 1177w, 969m, 858w, 733m, 713m and 355m;[12] δ_H(200 MHz; CD_3COCD_3) 3.84 (3 H, s) and 6.37 (1 H, br s); δ_C(50 MHz; CD_3COCD_3, internal reference: the center line of the CD_3COCD_3 heptet: 30.50 ppm) 160.72, 159.78 and 54.02; *m*/*z* (EI) 60 (16%), 59 (45), 45 (100), 44 (30) and 43 (6).

Methyl 3-diazo-2-oxopropanoate 14[13]

Compound **14** was obtained (65% yield) as a pale yellow solid; mp 104 °C;[13] ν_{max}(pellet)/cm^{-1} 3108s, 2142m, 2110m, 1730s, 1626s, 1455w, 1379m, 1277s, 1134w, 1066w, 960w, 891m, 793w, 598w and 561w;[13] δ_H(200 MHz; $CDCl_3$) 3.90 (3 H, s) and 6.20 (1 H, s);[13] δ_C(50 MHz; $CDCl_3$) 176.47, 160.77, 57.09 and 53.37; *m*/*z* (EI) 128 (M^+, 62%), 98 (19), 69 (100), 59 (18) and 41 (22).

1,4-Bis(diazo)butane-2,3-dione 15[14]

Compound **15** was obtained (30% yield) as yellow crystals; mp

124 °C;[14] ν_{max}(pellet)/cm^{-1} 3135m, 2118s, 1617s, 1319s, 1133w, 1092w, 989w, 934w, 806m, 585w, 560m and 432w;[14,15] δ_H(200 MHz; $CDCl_3$) 6.22 (2 H, s); δ_C(50 MHz; $CDCl_3$) 181.36 and 52.83; *m*/*z* (EI) 138 (M^+, 79%), 69 (100), 54 (7), 53 (16) and 41 (26).

Reaction of ethanedioyl dichloride 4a and H_2O

In preliminary tests we observed the behaviour of a $CDCl_3$ solution of $(COCl)_2$ **4a** in the presence of an equimolecular amount of H_2O at −30 °C: at this temperature the solubility of H_2O in $CDCl_3$ may be modest and several hours were allowed for any reaction eventually to take place in the rotating NMR tube kept at constant temperature. A very slow decomposition with formation of CO_2 (peak at 124.55 ppm)[16] as the only detectable product was observed, while the concentration of the substrate decreased, as could be monitored from the intensity ratio of the signals of the solvent *vs.* the $(COCl)_2$ peak (159.46 ppm). The same experiment run in CD_3CN, where H_2O is definitively fully soluble under the reaction conditions, showed an even slower decomposition rate of **4** (160.70 ppm) to CO_2 (125.26 ppm). In this context, $(CO_2H)_2$ was found to be very insoluble in $CDCl_3$ (or CD_2Cl_2): only when Et_2O was added were reasonable concentrations achieved for a suitable NMR observation, the corresponding ^{13}C peak being found at 158.86 ppm.[17]

Ethanedioic acid anhydride 1 ‡

Ethanedioyl dichloride (**4a**, 2.3 mmol) or bromide (**4b**, 2.3 mmol) was admitted through a rubber seal in one portion at −30 ± 5 °C, under efficient magnetic stirring in a dry Ar atmosphere to a suspension of finely ground anhydrous $Ag_2C_2O_4$ (3.0 mmol) in dry Et_2O (3 ml) in a 5 ml round bottomed flask. The heterogeneous reaction mixture was stirred during 1 h between −15 and −10 °C, then chilled at −20 °C and quickly filtered through a Luer-lock syringe connected to a stainless steel 13 mm holder assembly, equipped with PTFE 5.0 µm pores filters (Millipore SpA, Vimodrone, MI, Italy), to free it from formed AgCl (or AgBr) and excess $Ag_2C_2O_4$. The solvent, as well as unreacted dihalide **4**, were stripped off *in vacuo* at *ca.* −15 °C (25 Pa, 5 min) and the white solid residue was taken up with $CDCl_3$ (0.4 ml) and Et_2O (0.2 ml), because $CDCl_3$ alone proved to be an unsatisfactory solvent for the product: the obtained clear solution was suitable for obtaining NMR data, which were collected at −30 °C. When analyzed by ^1H NMR, only signals due to the solvents were detectable; the ^{13}C NMR spectrum was found to exhibit, beside the solvents signals, the occurrence of an intense peak at 144.85 ppm (Fig. 1). A similar reaction performed with **4b** gave exactly the same result. Peaks for CO and CO_2 were not present in the spectra of these reactions, ruling out the formation of these two products as the overall result of the interaction of $(CO_2Ag)_2$ (**8**) with any ethanedioyl dihalide. On the other hand, prompt gas evolution (CO and CO_2), apparently initiating at *ca.* 0 °C, was observed when the mixture was left standing at room temp.: eventually the peak at 144.85 ppm faded completely. When the reaction mixture was first filtered from all possible insoluble reactants and products, the solvent was evaporated *in vacuo* at low temperature and the residue allowed to warm up to room temp., either at reduced pressure when connected to the direct inlet unit of the mass spectrometer with continuous monitoring of the vaporized material, or in a sealed vessel under He atmosphere with continuous headspace gas analysis by GC–MS, no trace of **1** could be detected and the gas phase analysis was found to contain CO and CO_2 in the ratio *ca.* 1 : 1. GC–MS analyses of the filtered reaction mixtures were also always secured, but, aside from traces of unreacted **4**, only CO and CO_2 could be detected. It is noteworthy that the acid **7** and its dichloride **4a** (or dibromide **4b**, 155.82 ppm) under the conditions described above did not react to give any ^{13}C NMR observable new product at −30 °C, either in $CDCl_3$–Et_2O or in CD_2Cl_2–Et_2O.

Reaction of ethanedioic acid anhydride 1 and MeOH

The solution of the anhydride **1**, prepared as described above, was treated, after monitoring by ^{13}C NMR, with a calculated deficient amount of anhydrous MeOH (10 µl) at −30 °C directly into the NMR tube. Immediate ^1H NMR spectroscopic analysis showed (alongside remnants of **1,** from ^{13}C NMR, 145.07 ppm) the complete disappearance of MeOH and peaks for at least two novel products with singlets at 13.80 (broad, highly acidic protons), 3.99 and 3.98 ppm (Fig. 2), the latter two peaks showing an integral ratio of 3 : 7. The ^{13}C NMR spectrum (Fig. 3), in which a signal for **7** (158.79 ppm), probably due to some unavoidable hydrolysis, was also present, exhibited four main peaks in the carbonyl region at 155.88, 155.58, 151.91 and 150.79 ppm and, in addition, two sharp peaks in the CH_3OCO region at 54.64 and 54.23 ppm, in the approximate ratio 3 : 7. These latter two signals were assigned to methyl carbons and correlated with those present in the proton spectrum at 3.99 and 3.98 ppm by appropriate DEPT and H,C-COSY experiments. In the carbonyl region, a number of minor peaks were also present (Fig. 3). The same experiment carried out with deficient, but more abundant MeOH (20 µl), which reacted completely as well as did the starting material **1**, gave essentially the same results, but the relative amount of the product **11**, characterized by the peaks at 3.99 (H) and 54.64 (C) ppm was sharply reduced to some 15%. Peaks for ethanedioic acid monomethyl ester (**10**, $\delta_H = 3.88$ ppm; $\delta_C = 158.22$, 157.47 and 52.97 ppm) and ethanedioic acid dimethyl ester (**12**, $\delta_H = 3.90$ ppm; $\delta_C = 157.08$ and 53.11 ppm) started to become evident and these compounds were found in essentially equimolar amounts; whereas the presence of ethanedioic acid **7** appeared enhanced. Compounds **7**, **10** and **12** were the only ones detected when excess MeOH was used on **1**: in this case the monoester **10** was slightly more abundant than the diester **12** (6 : 4). In a similar experiment with deficient MeOH, such that some **9b** and **11** survived, the solution was left to reach room temp. (gas evolution set in) and kept 10 h with occasional stirring: compounds **9b** and **11** were then completely absent.

Reaction of ethanedioic acid anhydride 1 and CH_2N_2

The white solid residue from a standard preparation of **1** (see above) was dissolved in Et_2O (5 ml) and treated with an excess of a dry ethereal solution of CH_2N_2,[8] under stirring during 15 min at −15 °C. The reaction mixture was allowed to reach room temp. and then additionally stirred for 15 min. The excess reagent and Et_2O were carefully distilled off and the residue was taken up with $CDCl_3$ (0.5 ml) for ^1H and ^{13}C NMR analysis. The following products were present and identified by comparison with authentic materials: 1,4-bis(diazo)butane-2,3-dione (**15**, $\delta_H = 6.26$ ppm; $\delta_C = 181.28$ and 52.89 ppm); methyl 3-diazo-2-oxopropanoate (**14**, $\delta_H = 6.24$ and 3.90 ppm; $\delta_C =$ 176.41, 160.68, 57.05 and 53.23 ppm); ethanedioic acid dimethyl ester (**12**, $\delta_H = 3.92$ ppm; $\delta_C = 157.79$ and 53.44 ppm). The ratio of **15** : **14** was estimated from integrals as 3 : 7.

Acknowledgements

This work was supported in part by grants to A. G. G. (CNR 95.01044CT03, 96.02740CT03, 97.02807CT03) and to P. S. (MURST 1994, 40%). We are indebted to Dr P. Martinuzzi for NMR recording and Mr V. Tosoratti for skillful assistance.

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‡ IUPAC name: 1,4-dioxane-2,3,5,6-tetrone.

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Paper 8/03430C
Received 6*th May* 1998
Accepted 18*th June* 1998