

The dimer of phenylpropiolyl chloride

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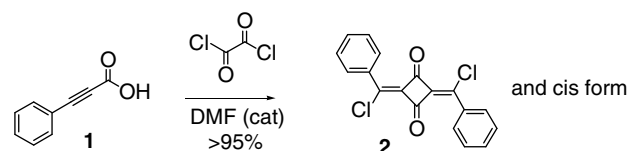
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Abstract

Arylpropiolyl chlorides undergo dimerization to a mixture of *cis*- and *trans*-alkylidenecyclobutane-1,3-diones. The structures of these products have been established by an X-ray study of the crystalline products formed by repeated crystallization or, alternatively, by thermal gradient sublimation.

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Acetylenic acid chlorides have long been known for their high reactivity and tendency to decompose upon storage.^{1–4} During the preparation of phenylpropiolyl chloride from thionyl chloride and phenylpropionic acid **1**, it was observed that distilled samples of the yellow liquid acid chloride gradually solidified to a brick-red semi-crystalline mass over a period of weeks.⁵ When this material was recrystallized from benzene it formed beautiful deep red crystals, mp 175–175.5 °C (45%). Elemental analysis and molecular weight determination showed the red product to be a dimer of phenylpropiolyl chloride, while a recent ¹³C NMR spectrum analysis revealed a 60–40 mixture of two very similar compounds. An independent X-ray crystallographic determination⁶ has now established the structure of the dimer to be **2** (Scheme 1). This single crystal form, obtained by slow sublimation, is quite unusual in that the unit cell contains 3 molecules: two molecules with the chlorine atoms ‘*cis*’, (Fig. 1a), and one molecule with the chlorine atoms in the ‘*trans*’ configuration (Fig. 1b). Before the availability of the NMR data, we were uncomfortable with our structural assignment in light of a dipole



Scheme 1.

moment measurement of 2.7 D⁷ and an earlier X-ray study of a monoclinic crystal obtained via repeated recrystallization that contained only the ‘*trans*’ isomer.⁸ The more recent thermal gradient sublimation also produced red plates. A single crystal determination now shows these plates to be a different crystal form (triclinic) consisting solely of *trans*-**2**.⁶

To see if *cis*-**2** has a dipole moment that is in accord with the observed value for a mixture of *cis*- and *trans*-**2**, calculations were carried out at the B3LYP/6-311+G* level using the B3LYP/6-31G* geometries. As expected, the calculated energies were similar, with *cis*-**2** having an energy only 0.6 kcal/mol greater than that for *trans*-**2**. The calculated dipole moment of *cis*-**2** was 4.09 D, in accord with the observed value of 2.7 D for the *cis*/*trans* mixture.

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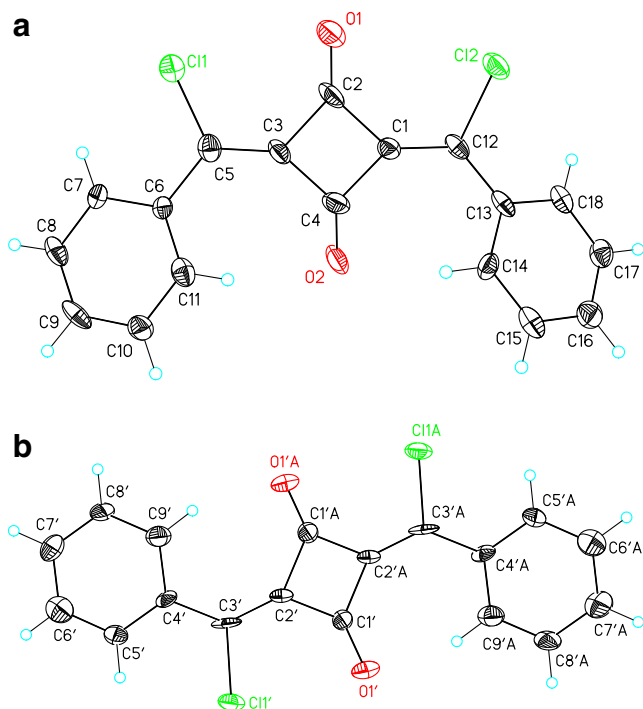
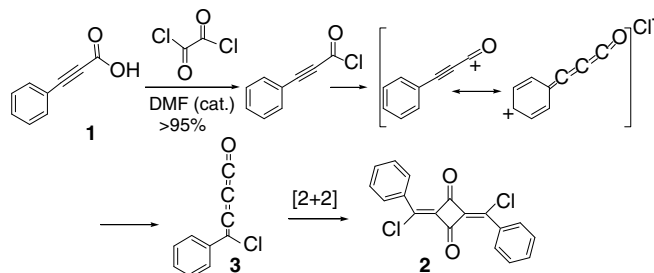


Fig. 1. (a) View of *cis*-**2** in the mixed crystal, showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. (b) View of *trans*-**2** in the mixed crystal showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The molecule lies around a crystallographic inversion center at $-1/2, 0, 0$. Atoms with labels appended by A are related by $-1-x, -y, -z$.

We have found that phenylpropiolyl chloride prepared with oxalyl chloride is particularly prone to dimerization, and distillation can lead to an uncontrolled reaction. From our experience, thionyl chloride is a better choice for the preparation of distilled arylpropiolyl chlorides. Near quantitative yield of dimer **2** can easily be obtained in days without distillation by the reaction of oxalyl chloride and a catalytic amount of dimethylformamide with phenylpropionic acid followed by solvent removal (Supplementary data).

The possibility that the reaction might be free radical in nature was considered when, on one occasion, dimerization took place with almost explosive force during redistillation

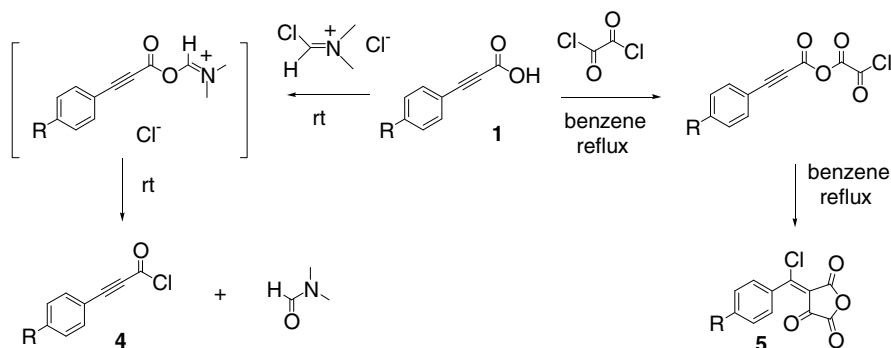


Scheme 2.

of phenylpropiolyl chloride. Free radical traps such as BHT and free radical initiators (AIBN, benzoyl peroxide, and *t*-butyl peroxide) had no effect on the rate of dimer formation. In addition, acids ($\text{BF}_3 \cdot \text{Et}_2\text{O}$, AlCl_3 , H_2SO_4 , and HCl) as well as light and moisture all failed to increase the rate of dimer **2** formation. On the other hand, heat accelerates the dimerization significantly, and most importantly, the dimer only forms in good yield with neat samples of highly pure acid chloride (or DMF catalysis).

These observations have led us to propose a benzyldieneketene intermediate **3**, which can be formed with the participation of the aromatic ring (Scheme 2). Rapid [2+2] cycloaddition of **3** provides **2** directly. In support of this pathway is the more facile dimerization of *p*-methoxypropiolyl chloride and our failure to observe any of this reaction mode with *p*-nitrophenylpropiolyl chloride. In addition, no [2+2] dimerization was observed with propiolyl chloride, trimethylsilylpropiolyl chloride or butaniolyl chloride.

Crombie, et al.,⁹ have examined the reaction of some phenylpropionic acids bearing electron-releasing groups such as 3,4-methylenedioxy, 3,4,5-trimethoxy, and 3,4-dimethoxy with oxalyl chloride in benzene at reflux. This reaction took a different course, yielding a chloro-arylidene-tetrahydrofuran-2,4,5-trione, **5** (Scheme 3). They have proposed that the reaction involves the cyclization of an intermediate mixed anhydride with oxalyl chloride under conditions that are quite different from those in the present work. The fact that the formation of **5** is not observed in our work may be due to the powerful catalytic



Scheme 3.

activity of DMF, which does not favor the formation of an oxalyl chloride-mixed anhydride intermediate. A control reaction, in which phenylpropionic acid **1** was treated with oxalyl chloride in refluxing benzene by the method of Crombie, et. al.,⁹ turned reddish yellow during the 2 h reflux. However, ¹³C NMR analysis of the crude reaction mixture revealed no evidence for the formation of dimer **2**. This difference in reactivity may be explained by the reaction of DMF with oxalyl chloride to form the intermediate *N,N*-dimethylchloromethylenammonium chloride. This product¹⁰ converts phenylpropionic acid **1** to the acid chloride, **4** at room temperature thus eliminating the higher energy pathway to **5**. The acid chloride **4** is subsequently converted to dimer **2** as previously described in Scheme 3.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2008.01.115](https://doi.org/10.1016/j.tetlet.2008.01.115).

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7. We thank Professor J. D. Roberts for the dipole moment measurement.
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