Reactions of Diketen with Arenethiols: Preparation of Arylthioisocrotonic Acids and *S*-Aryl Thioacetoacetate Esters

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Summary The products formed by reaction of arenethiols with diketen in the presence of sulphuric acid are β-arylthioisocrotonic acids and not, as has been reported, *S*-aryl thioacetoacetates (which can be prepared by base catalysis).

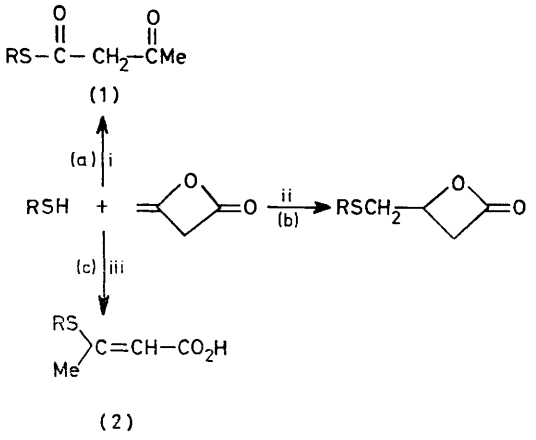
IN spite of the enormous literature on diketen,[1] little has been published on its reactivity towards thiols. Such reports as are available indicate that thiols cause the expected ring-opening of diketen to give *S*-aryl thioacetoacetate esters (**1**) [Scheme (a)].[2] In the presence of azobisisobutyronitrile (AIBN) and light, an anti-Markovnikoff, exocyclic addition has been observed[3] with aliphatic thiols [Scheme (b)]. We now report that reaction between arenethiols and diketen in the presence of H_2SO_4 gives arylthioisocrotonic acids (**2**)† and not, as claimed previously,[4] the *S*-aryl thioacetoacetates (**1**; R = Ph, C_6H_4-OMe-*m*, α-$C_{19}H_7$, or β-$C_{10}H_7$).

Compound (**1**; R = Ph) has been reported both as a solid,[4] m.p. 174·5—175·5 °C, and as a liquid[2b,c,5] which decomposes on attempted distillation. We have prepared (**1**; R = Ph) from diketen and benzenethiol under conditions reported as appropriate for activated aryl acetoacetates:[6] benzenethiol and diketen (1 : 1) were stirred together (ambient temperature, overnight) with one drop of triethylamine in dichloromethane and the solvent was removed at room temperature to give the product, colourless liquid, crude yield 95%, ν_{max} (neat) 1700 and 1725 cm^{-1} (2 × C=O); δ (60 MHz, CCl_4) 1·82 (s, enol-Me), 2·09 (s, keto-Me) (combined enol- and keto-Me, 3H), 3·57 (s, keto-CH_2), 5·39 (s, enol –CH=) (combined enol- and keto-resonances at δ, 3·57 and 5·39, *ca.* 1·5 H), and 7·32 (5H, m, ArH). The enol content (by n.m.r. integration) is 47%. Attempted distillation under reduced pressure led to dehydroacetic acid as reported previously.[2c,5] In sodium hydroxide solution (**1**; R = Ph) shows a transient absorbance, λ *ca.* 300 nm, measurable by stopped-flow spectrophotometry and ascribable to the rapidly hydrolysing enolate ion of the ester.‡ All these observations are consistent with structure (**1**). We have also prepared *S*-*p*-chlorophenyl thioacetoacetate, m.p. 45—46 °C, by this route; this compound has satisfactory elemental analyses (C, H, Cl), ^1H n.m.r. spectra (56% enol), and u.v. enolate ion absorbance (transient) around 300 nm and, on hydrolysis, produced *p*-chlorobenzenethiol quantitatively.

Route (c) (Scheme), using the literature procedure[4] [*viz.*, addition first of diketen and then 1 mol equiv. of H_2SO_4 to benzenethiol in ether (0—5 °C)], led to a white, crystalline solid (**3**), m.p. 175—177 °C (with bubbling),

† Autenrieth (ref. 7a) described the *E*-isomers of (**2**), with the hydrogen atom and arylthio group *cis* to one another, as β-phenylthioisocrotonic acids as opposed to the β-phenylthiocrotonic acids with the *Z*-configuration.

‡ The enolate ions formed (ref. 2d) by *S*-acetoacetyl-*N*-acetylcysteamine and *S*-acetoacetyl coenzyme A have λ_{max} 303 nm.



SCHEME. i, Base catalysis; ii, $h\nu$, azobisisobutyronitrile (AIBN); iii, Et_2O, H_2SO_4.

satisfactory elemental analysis for $C_{10}H_{10}O_2S$, δ (60 MHz, $CDCl_3$) 2·40 (3H, d, Me), 5·2] (1H, m, =CH–), and 7·45 (5H, m, ArH); ν_{max} 1675 cm^{-1} (C=O).§ However, no thiol was formed in base and no absorbance at *ca.* 300 nm (transient or otherwise) could be detected in alkali. Compound (**3**) is soluble in base, gives a red colouration in conc. H_2SO_4 solution, and evolves a gas on melting, properties which have been described for β-phenylthioisocrotonic acid[7] (**2**, R = Ph) a sample of which, prepared by an alternative route,[7] has m.p. 176·5—178·5 °C. A mixture of (**3**) and authentic (**2**, R = Ph) melted in the range 175·5—178 °C. The structure of the compound was established from its ^{13}C n.m.r. spectrum [20 MHz, $(CD_3)_2SO$, rel. to Me_4Si (multiplicities are with complete ^1H decoupling and with partial ^{13}C–^1H coupling)]: δ 19·5 (s and q, Me), 112·6 (s and d, CH), 129·3 (s and s, –C=), 130·2 (s and d, CH), 135·2 (s and d, CH), 147·0 (s and s, –S–C of Ph), and 165·5 (s and s, CO_2H) p.p.m. Compound (**2**; R = *p*-ClC_6H_4), m.p. 207·5—209 °C, has also been prepared with satisfactory elemental and spectroscopic analyses. Compound (**2**; R = Ph) exhibits a band at 2720 cm^{-1} in its i.r. spectrum ascribable to the carboxy OH group.

Thus the products from reaction of arenethiols with diketen in the presence of H_2SO_4 are not *S*-aryl thioacetoacetates as originally claimed[4] but, rather, the isomeric crotonic acid derivatives. The compound isolated using benzenethiol is identical with that described by Autenrieth[7] and we are currently studying stereochemistry about the C=C bond. It is interesting that ethyl β-phenoxyisocrotonate has been suggested as an intermediate in the Simonis reaction of ethyl acetoacetate with phenol in the presence of P_2O_5 to yield a chromone.[8] As far as we are aware, the reaction in the Scheme (c) is the first reported instance of alkenyl-oxygen ring-opening of diketen by nucleophilic species such as thiols.

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§ *Cf.* δ 2·38 (3H), 5·20 (1H), and 7·51 (5H); ν_{max} 1670 cm^{-1} (C=O) (ref. 4).

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