# Polyfluoro Carbonyl Compounds as Traps for Aryl-fused Cyclopropenones

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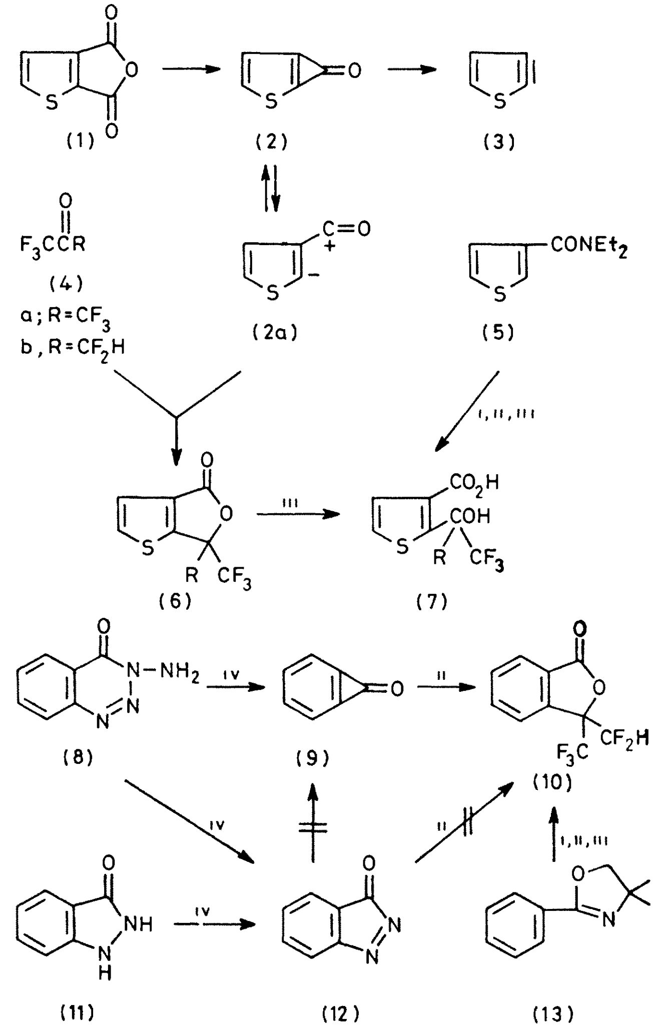
*Summary* Hexa- and penta-fluoroacetone effectively trap aryl-fused cyclopropenones either in the gas-phase or solution by means of a [3+2]-cycloaddition reaction giving $\gamma$-lactones.

IN connection with research on the generation of five-membered heteroarynes (**3**) from the gas-phase thermolysis of the corresponding anhydrides (**1**),[1] it was desirable to determine if, as has been proposed for phthalic anhydride,[2] an aroyl species with the composition and perhaps the structure† of a fused cyclopropenone such as (**2**), was an intermediate. The existence of the prototype benzocyclopropenone (**9**) from several other precursors has been postulated on the basis of matrix isolation[3] and trapping with several nucleophiles such as water,[4] acetic acid,[5] methanol,[4,5] and ammonia.[6] In the present instance, however, a trap was necessary which, in contrast with the substances used above, would be unlikely to react with the anhydride precursor (**1**)‡ and which furthermore would be reasonably volatile and thermally stable under the reaction conditions.[1] On the assumption that a species such as (**2**) might exhibit considerable dipolar character (**2a**) and thus be particularly prone to undergo [3+2]-cycloaddition reactions[8] with appropriate 1,3-dipolarophiles, a series of polyfluorocarbonyl compounds was considered for this purpose. Several such compounds (**4**) have been used previously to trap other dipolar, small ring species in solution.[9] This paper reports a significant extension of the utility of these compounds for trapping fused cyclopropenones in both the gas-phase and solution.

Gas-phase thermolysis[1] of the anhydride (**1**)[10] in the presence of hexafluoroacetone (**4a**) or pentafluoroacetone (**4b**) led to the formation of the noncrystalline adducts (**6a**)§ and (**6b**)§ in yields of 35 and 32%, respectively. The $\gamma$-lactone character of these adducts was established from their i.r. carbonyl frequency ($> 1800\ \text{cm}^{-1}$)[9] and saponification to their respective crystalline hydroxyacids (**7a**)§ and (**7b**),§ the latter of which was prepared by an independent synthesis from the diethylamide of 3-thenoic acid (**5**) by the procedure[11] shown in the Scheme. The possibility, as was demonstrated for nucleophilic traps,‡ that the polyfluorocarbonyl compounds (**4**) react directly with the anhydride (**1**) was rendered unlikely by the absence of any reaction between these compounds at temperatures below which (**1**) alone decomposes.



SCHEME. Reagents: i, BuLi, ii, (**4b**), iii, $H_3O^+$, iv, $Pb(OAc)_4$.

An example of the use of polyfluorocarbonyl compounds (**4**) for the solution trapping of fused cyclopropenones is provided by the formation of the lactone (**10**)§ in 4% yield from the oxidation of the benzocyclopropenone precursor (**8**) by $Pb(OAc)_4$ in the presence of (**4**) in methylene chloride.[4]

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† Both cyclic (refs. 3—5) and open structures (diradical and zwitterionic) (refs. 2, 4, and 6) have been considered for the species referred to as aryl-fused cyclopropenones in this paper. No structural implications should be drawn from this usage as the significance of this distinction is under investigation and will be discussed in a full paper.

‡ The anhydride (**1**) does react with nucleophiles under gas-phase pyrolysis conditions to give 3-thenoic acid derivatives consistent with the intermediacy of the cyclopropenone (**2**). Since, however, the same derivatives are obtained by decarboxylation of the half-acid formed by reaction of the nucleophiles directly with the anhydride (**1**), no conclusion regarding the existence of (**2**) is possible (ref. 7).

§ All new compounds displayed i.r., n.m.r., and mass spectral data consistent with their assigned structures. Satisfactory analyses were obtained for (**7a**) and (**7b**).

The structure of (**10**) was substantiated by synthesis from the phenyl oxazoline (**13**)[12] as shown in the Scheme. The low yield of the lactone (**10**) is comparable to that for other benzocyclopropenone-derived products obtained from the precursor (**8**).[4] The possibility that the lactone (**10**) might arise from the indazolone (**12**), a known intermediate in the oxidation of (**8**),[4] was eliminated by the failure to detect (**10**) from the oxidation of (**11**),[13] an alternate precursor of (**12**), in the presence of (**4b**).

The above results demonstrate the utility of polyfluorocarbonyl compounds such as (**4**) as gas-phase and solution traps for fused cyclopropenones generated from a variety of precursors.

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