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THALLATION-IODINATION STUDIES OF DIARYLKETONES

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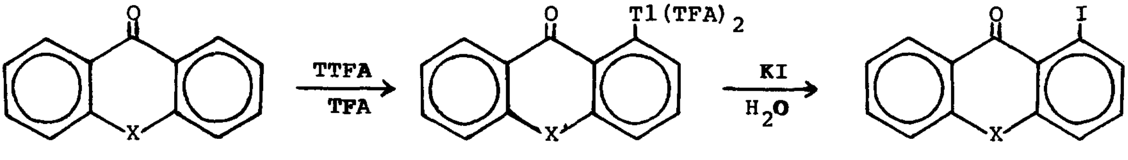
In an effort to derivatize 2,2'-bridged benzophenones (1) *ortho* to the carbonyl group, we decided to study electrophilic substitution by thallium of diarylketones[1,2]. Although an *ortho*-orientation effect in this reaction is well known for acids and esters[3], ketones had not been reported in this context.

Benzophenone, as the simplest representative of the substrates tested, proved to be totally unreactive toward thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA) at reflux. Attempting to minimize steric effects we then tried fluorenone, but also without success. Anthrone, however, reacted at room temperature with TTFA/TFA giving a 76% yield of anthraquinone. Although unexpected, this result is easily rationalized by assuming enolization to anthrol which is then oxidized in a manner analogous to that of phenols[4]. In order to avoid this tautomerization, we prepared and tested 10,10-dimethylanthrone (1a)[5]. Treatment of 1a with TTFA/TFA resulted in thallation at the 1-position (2a), which followed by treatment with aqueous potassium iodide[6] led in 29% yield to 1-iodo-10,10-dimethylanthrone (3a). Similar treatment of dibenzosuberone (1b) gave 4-iododibenzosuberone (3b) in 71% yield.

Extending the procedure to heterocyclic systems, thioxanthone (1c) afforded 1-iodothioxanthone (3c) (18% yield), whereas xanthone and N-methylacridone were unreactive under the same conditions.



1a-1c   2a-2c   3a-3c

a, X = $C(CH_3)_2$; b, X = $-CH_2CH_2-$; c, X = -S-

Conditions for the transformations of substrates 1a-1c are presented in Table I. Yields are based upon direct treatment of the intermediate TFA solutions of arylthallium ditrifluoroacetates (2a-2c) with aqueous potassium iodide. Separate reactions were used to obtain samples of the thallated intermediates.

Table I. Conditions for the Thallation-Iodination of Ketones **1a**-**1c**.

Substrate	TTFA/Subst	Time(h)	Temp(°C)	Product(%yield)[a]	mp(°C)[b]
1a	10:1	96	23	**3a** (29)	166-8
1b	1:1	48	23	**3b** (71)	127-8
1c	1:1	31	73	**3c** (18)	138-40

a) Satisfactory elemental analyses (C&H) were obtained.

b) Recrystallized from EtOH; melting points are uncorrected.

The structures of these iodoketones (**3a**-**3c**) were readily confirmed by PMR analysis of both final products and the crude thallated intermediates. Reasons for the considerable variation in substrate reactivity are not clearly obvious, but, where applicable, this method provides a very simple and direct route to otherwise difficultly prepared substances.

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