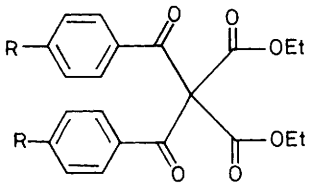
# Reinvestigation of a Reported Synthesis of a Series of Tetracarbonylmethanes

**E. Lee-Ruff,* P. Kwong, and A. C. Hopkinson**

*Department of Chemistry, York University, North York, Ontario, Canada M3J 1P3*

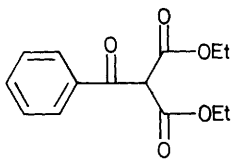
Previously reported tetracarbonylmethanes obtained from bis-acylations of bromomalonate with tri-n-butylarsine have been shown to be enol esters.

Our interest in carbocations substituted by electron-withdrawing groups such as carbonyl and thiocarbonyl[1,2] drew our attention to a recent report by Shen and Yang[3] on the preparation of a series of tetracarbonylmethanes derived from a novel bis-acylation of bromomalonate *via* halophilic reaction of tri-n-butylarsine. With the purpose of using these derivatives as possible precursors to tricarbonyl substituted carbocations, we repeated their procedures for the preparation of (**1a** and **b**).



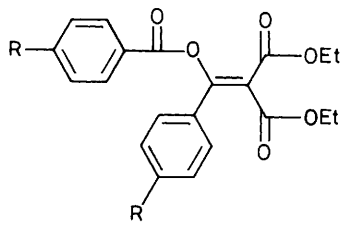
(1)

**a** ; R = H
**b** ; R = $NO_2$



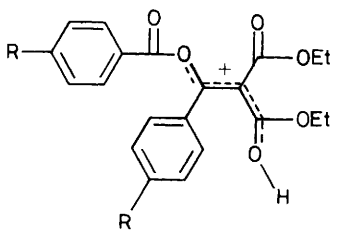
(2)

**a** ; R = H
**b** ; R = $NO_2$



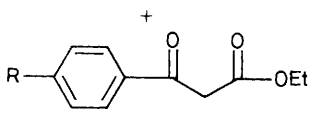
(3)

**a** ; R = H
**b** ; R = $NO_2$



(4)

**b** ; R = $NO_2$

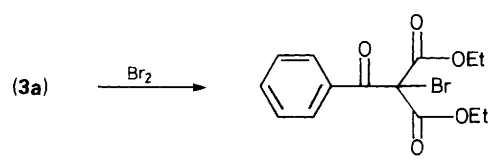


(5)

**a** ; R = H

This was carried out by the addition of the aroyl chloride (1 equiv.) to a mixture of diethylbromomalonate (1 equiv.) and tri-n-butylarsine (1 equiv.) under nitrogen and heating the mixture to 80 °C. The reaction time for (**1a**) was slightly longer (6 h) than reported as was evident by monitoring the disappearance of bromomalonate by $^1H$ NMR spectroscopy. In addition to the reported product (**1a**) (34%), the monobenzoyl malonate derivative was obtained in 28% yield. The purported derivative (**1b**) was obtained in 71% yield† (m.p. 96—97 °C, lit. m.p.[3] 95—96 °C). It was evident from preliminary analysis of the high-field $^1H$ and $^{13}C$ NMR spectra that the *original* structure assignments of (**1a** and **b**) were *inconsistent* with the spectral data. In both the $^1H$ and $^{13}C$ NMR spectra of (**1b**) and in the $^{13}C$ NMR spectrum of (**1a**) two different ethoxy ester groups are discernible. We propose that the correct structures of these compounds are actually the enol esters (**3a** and **b**) and that the whole series of reported tetracarbonylmethanes are most likely the related enol esters (**3**).

Evidence for structures (**3a** and **b**) was based on both spectral data and chemical transformations. The $^1H$ and $^{13}C$ NMR spectral‡ of (**3a** and **b**), in addition to exhibiting peaks associated with two non-equivalent ethoxyl ester groups, showed peaks in the aromatic region indicating the presence of two non-equivalent aryl groups. This was particularly evident in the case of the *p*-nitro derivative (**3b**) in which four pairs of doublets (two pairs superimposed) are discernible in the $^1H$ NMR spectrum. Furthermore, four peaks are present in the region δ 159—167 associated with the presence of three non-equivalent carbonyl carbons and one enol carbon in the $^{13}C$ NMR spectrum of (**3a**). The symmetry associated with structures (**1a** and **b**) is inconsistent with the observed NMR data. In order to ensure that local asymmetry in (**1a** and **b**), perhaps arising from restricted bond rotation, is not the origin of the multiplicity of peaks, the NMR spectra were recorded over the temperature range 25—85 °C with no observable changes.

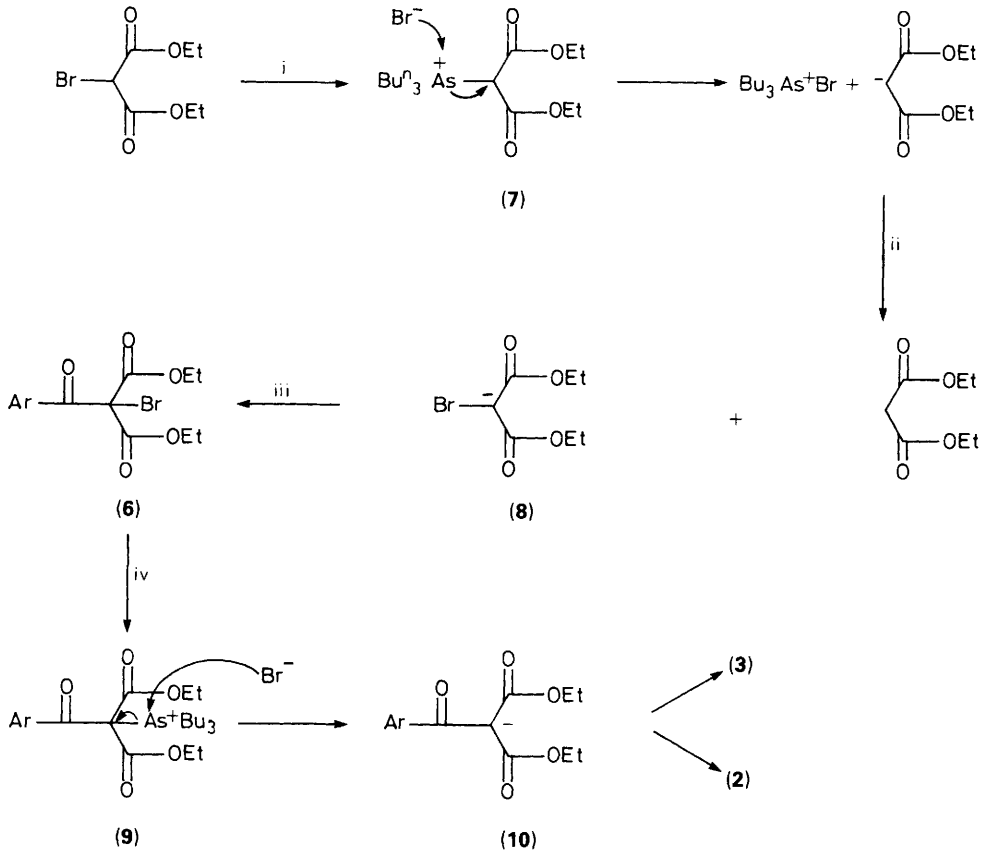


(**3a**)

(6a)

† All new compounds gave satisfactory molecular parent ions in the mass spectra and satisfactory elemental analyses.

‡ All spectra were recorded at 300 MHz on a Bruker AM-300 spectrometer.




**Scheme 1.** *Reagents*: i, Bu$^n_3$As; ii, bromomalonate; iii, ArCOCl; iv, Bu$^n_3$As.

Even more compelling evidence for the assignments of (**3a** and **b**) was obtained from their acid hydrolysis products. Hydrolysis of (**3b**) with $ClSO_3H$ at −50 °C followed by quenching with aqueous bicarbonate gave (**2b**) and *p*-nitrobenzoic acid as the only products. Hydrolysis of (**3a**) in 96% $H_2SO_4$ followed by quenching with water gave ethylbenzoyl acetate (**5a**) and benzoic acid as the only products. Under the same conditions (**2a**) undergoes decarboxylation to (**5a**). Bromination of (**3a**) gave the benzoylbromomalonate (**6a**) and benzoic acid after work-up. All of these observations are consistent with the labile nature of enol esters towards acid hydrolysis[4] and bromination,[5] and inconsistent with the expected reactivity of the tetracarbonylmethane derivatives (**1a** and **b**). The low temperature (−50 °C) $^{13}C$ NMR spectrum of (**3b**) in $ClHSO_3$ showed the production of ion (**4b**), again clearly indicating the presence of two non-equivalent ethoxy ester and aryl groups. The downfield shifts of both the methylene and methyl signals of only one of the ethoxy groups in the $^{13}C$ and $^1H$ NMR spectra of (**3b**) in $ClSO_3H$ is indicative of mono-protonation.

Although no mechanism for the bis-acylation was presented in the original report,[3] the formation of diethylmalonate as a byproduct was indicated in their reaction scheme. We have confirmed the formation of diethylmalonate and its simultaneous production in equimolar amounts with production of (**3**). The possibility of the bis-acylation arising from an arsonium ylide[6] cannot be ruled out although such an intermediate could not account for the concomitant production of diethylmalonate. We propose that the arsonium salt (**7**) (Scheme 1) is most likely the enolate precursor of diethyl malonate from bromide ion displacement of malonate in (**7**). The bromoenolate (**8**), formed by proton-transfer with the malonate ion formed, could undergo mono-acylation to give the aroylbromomalonate (**6**) which is subsequently transformed to the arsonium salt (**9**). The latter acts as the enolate precursor to the observed bis-acylation products (**3**). The aroyl malonate ion (**10**) is generated from bromide ion displacement of the arsonium salt (**9**). That *O*-acylation takes place in preference to *C*-acylation is associated with the steric encumbrance of derivatives (**1**) and the π-conjugative stability of the enol esters (**3**). *O*-Acylation at the ester carbonyl is not as likely as at the ketone carbonyl due to the greater basicity of keto carbonyl oxygen centres.[7]

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