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 Yang³ 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).

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 monobenzovl malonate derivative was obtained in 28% vield. 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 ¹³C NMR spectra that the *original* structure assignments of (1a and b) were inconsistent with the spectral data. In both the ¹H and ¹³C 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 ¹³C 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 ¹³C 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.



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

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



Scheme 1. Reagents: i, Bun₃As; ii, bromomalonate; iii, ArCOCl; iv, Bun₃As.

Even more compelling evidence for the assignments of (3a and b) was obtained from their acid hydrolysis products. Hydrolysis of (3b) with ClSO₃H at -50 °C followed by quenching with aqueous bicarbonate gave (2b) and p-nitrobenzoic acid as the only products. Hydrolysis of (3a) in 96% H₂SO₄ 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 hydrolysis⁴ and bromination,⁵ and inconsistent with the expected reactivity of the tetracarbonylmethane derivatives (1a and b). The low temperature $(-50 \,^{\circ}\text{C})^{13}\text{C}$ NMR spectrum of (3b) in ClHSO₃ 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 ¹³C and ¹H NMR spectra of (3b) in ClSO₃H 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 ylide⁶ 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

The authors thank the Natural Sciences and Engineering Research Council (N.S.E.R.C.) of Canada for financial support.

Received, 21st August 1989; Com. 9/03579F

References

- 1 X. Creary, A. C. Hopkinson, and E. Lee-Ruff, in 'Advances in Carbocation Chemistry,' vol. 1, ed. X. Creary, JAI Press, 1989, pp. 45-92.
- 2 D. Fletcher, F. J. Ablenas, A. C. Hopkinson, and E. Lee-Ruff, Tetrahedron Lett., 1986, 27, 4853.
- 3 Y. Shen and B. Yang, J. Chem. Soc., Chem. Commun., 1988, 1394.
- 4 E. K. Euranto, Pure Appl. Chem., 1977, 49, 1009.
- 5 C. A. Horiuchi and J. Y. Satoh, Synthesis, 1981, 312.
- 6 M. Shao, X. Jin, Y. Tang, Q. Huang, and Y. Huang, *Tetrahedron Lett.*, 1982, 23, 5343.
- 7 J. March, 'Advanced Organic Chemistry,' Wiley, 1985, p. 220.