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^{1}H-NMR study of some new acetyl dimethylbiphenyls: unambiguous signal assignment for the methyl groups

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Abstract. The abundance ^{1}H-NMR spectra of some new mono- and diacetyl compounds derived from 2,2′-dimethyl-, 3,3′-dimethyl-, and 4,4′-dimethylbiphenyls were recorded. Unambiguous signal assignment of the methyl groups of the aromatic biphenyl rings were made for the structure elucidation.

1. Introduction

Aromatic derivatives with substituents containing an sp^2 hybridised carbon have been the subject of numerous investigations [5]. In aromatic molecules, the change in the proton chemical shifts has been shown to be proportional to the change in the π-electron charge density on the carbon atom to which the hydrogen is bonded [11]. Nomura and Takeuchi [12] studied the role of the inductive (or field) effect of the substituent on the proton chemical shifts in mono-substituted m-xylenes.

Dimethylbiphenyls **1a**, **1b** and **1c** are reported to give a mixture of isomers on sulphonation [9], chlorination [2,3], bromination and iodination [18] and nitration [10]. The product composition from the sulphonation reaction was determined from the ^{1}H-NMR spectrum of the reaction mixture [9]. In this study we report some ^{1}H-NMR spectral data to characterize the structure of the mono- and diacetyl derivatives obtained by the Friedel–Crafts acetylation of hydrocarbons **1a**, **1b**, and **1c** (Fig. 1).

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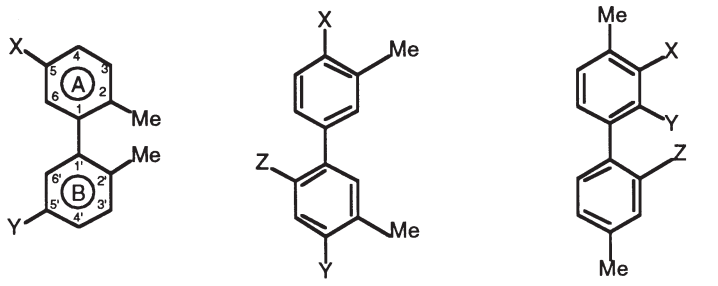

Series a
1a X=Y=H
2a X=Ac;Y=H
3a X=Y=Ac

Series b
1b X=Y=Z=H
2b X=Ac; Y=Z=H
3b X=Y=Ac; Z=H
4b X=Z=Ac; Y=H

Series c
1c X=Y=Z=H
2c X=Ac; Y=Z=H
3c X=Z=H; Y=Ac
4c X=Z=Ac; Y=H

Fig. 1.

2. Experimental

IR spectra were measured as KBr discs for crystalline ketons, or thin films for oily ketones on a Pye Unicam SP3-100 spectrophotometer. The proton NMR spectra were recorded on a Varian FT-80 A spectrometer at 80 MHz for solutions in deuteriochloroform solution, at 5% concentration, with tetramethylsilane as internal standard. GLC analyses were performed with a stainless steel column packed with SE30 (10%) at 250° on a Pye Unicam 204 with a Pye Unicam DP 88 electronic integrator. Compounds **1a**, **1b** and **1c** were commercially available from Aldrich. All mono- and diacetyl compounds in Table 1 were new and synthesized by the Friedel–Crafts acetylation reactions[1] of hydrocarbons **1a**–**c**, and show on GLC a purity $> 99\%$, and gave a satisfactory elemental analysis. All solvents were dried prior to use in the acetylation reactions.

3. Results and discussion

The [1]H-NMR chemical shifts of the methyl protons could be used as an indication for the position of substitution of an acetyl or a methyl group linked to the aromatic nucleous [1,8], viz. the δCH_3 in toluene [7] is 2.34 ppm. Substitution of an acetyl group ortho to the methyl group will shift δCH_3 downfield to 2.85 ppm, while for meta- or para-substitution, the values are 2.27 and 2.52 ppm respectively. Analysis of the δCH_3 values in Table 2 reveal significant variation in the aromatic methyl proton chemical shifts. In series **c**, the absorption of the methyl group in the 4-position for ketone **2c** and **4c** is shifted to downfield by 0.41 and 0.40 ppm respectively, i.e., $\Delta\delta$(**2c**–**1c**) $= 0.41$ ppm and $\Delta\delta$(**4c**–**1c**) $= 0.40$ ppm. Downfield shifts can be ascribed to the electron withdrawing inductive [6] effect of the ortho acetyl group at the 3-position. Substituting an acetyl group at the 2′-position has very little effect on the chemical shift of the 4′-methyl protons. Not unexpectedly, an acetyl group at the 2-position in **3c** will have no significant effect on δCH_3 of the 4-methyl protons. On the contrary, a benzoyl group at this position will show some effect on δCH_3 of the methyl protons [14]. Further support for this positional assignment comes from the intense IR absorptions. The ν_{co}

[1]Unpublished results.

Table 1
Physical and spectral data for mono- and diacetyl compound prepared

Compound	mp (°C)	Molecular formula*	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
2a	oil	$C_{16}H_{16}O$ (224.3)	2.05 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 7.38 (m, 5H, H-arom), 7.64 (d, 1H, H-4, J=9.0), 7.92 (m, 1H, H-6)
3a	140–141	$C_{18}H_{18}O_2$ (266.3)	2.11 (s, 6H, $2CH_3$), 2.59 (s, 6H, $2CH_3CO$), 7.34 (m, 4H, H-arom), 7.78 (m, 2H, H-arom)
2b	oil	$C_{16}H_{16}O$ (224.3)	2.43 (s, 3H, CH_3), 2.56 (s, 3H, CH_3CO), 2.58 (s, 3H, CH_3), 7.35 (m, 6H, H-arom), 7.76 (d, 1H, H-6, J=9.0)
3b	129–131	$C_{18}H_{18}O_2$ (266.3)	2.56 (s, 6H, $2CH_3CO$), 2.58 (s, 6H, $2CH_3$), 7.46 (m, 4H, H-arom), 7.61 (d, 2H, H-6, H-6′, J=9.0)
4b	68–69	$C_{18}H_{18}O_2$ (266.3)	2.39 (s, 3H, CH_3), 2.49 (s, 3H, CH_3CO), 2.56 (s, 3H, CH_3CO), 2.58 (s, 3H, CH_3), 7.31 (m, 4H, H-arom), 7.50 (d, 1H, H-5′, J=9.0), 7.72 (d, 1H, H-5, J=9.0)
2c	oil	$C_{16}H_{16}O$ (224.3)	2.14 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.55 (s, 3H, CH_3CO), 7.34 (m, 6H, H-arom), 7.75 (d, 1H, H-2, J=1.9)
3c	oil	$C_{16}H_{16}O$ (224.3)	2.10 (s, 6H, $2CH_3$), 2.49 (s, 3H, $2CH_3CO$), 7.29 (m, 6H, H-arom), 7.53 (d, 1H, H-3, J=1.9)
4c	55–56	$C_{18}H_{18}O_2$ (266.3)	2.07 (s, 3H, CH_3), 2.49 (s, 3H, CH_3CO), 2.50 (s, 3H, CH_3), 2.57 (s, 3H, CH_3CO), 7.24 (m, 4H, H-arom), 7.48 (d, 1H, H-2, J=2), 7.72 (d, 1H, H-3′, J=1.9)

* Satisfactory microanalysis obtained: C±0.32, H±0.24.

Table 2
^{1}H-NMR chemical shifts (ppm from TMS) of acetyl group* and methyl of the biphenyl ring

Compound	δ_2	δ_3	δ_4	δ_5	δ_6	δ_2'	δ_3'	δ_4'	δ_5'	δ_6'
1a	2.02					2.02				
2a	2.12			2.57*		2.05				
3a	2.11			2.59*		2.11			2.59*	
1b		2.43					2.43			
2b		2.58	2.56*				2.43			
3b		2.58	2.56*				2.58	2.56*		
4b		2.58	2.56*				2.39			2.49*
1c			2.10					2.10		
2c		2.55*	2.51					2.14		
3c	2.49*		2.10					2.10		
4c		2.57*	2.50			2.49*		2.07		

values for the 3-acetyl in **2c** and **4c** are 1678 and 1676 cm^{-1} respectively, while those for the 2′- and 2-acetyl groups in **2c** and **4c** are 1685 and 1689 cm^{-1} respectively. The latter values indicate clearly a sterically hindered carbonyl group. These assignments illustrate the dominating influence of the methyl substituent at the 4-position which stablizes hyperconjugatively the σ-complex leading to 3-acetylation as in **2c** and **4c** respectively.

Examination of the data in Table 2 thus showed that the δCH_3 for the 3-methyl in compounds **2b**, **3b** and **4b**, and 3′-methyl in **3b** (series **b**, Fig. 1) is shifted to downfield by 0.15 ppm relative to **1b**, while that for the 3′-position in **2b** and **4b** shows little variation. The same arguments could be used to confirm the structure of the ketones **2b**, **3b** and **4b**, which exhibited intense IR absorption (ν_{CO}) for the acetyl group at 1680, 1684 and 1683 cm^{-1} respectively, and that of the 4′-acetyl in **3b** at 1684 cm^{-1}, while the absorption of the 6′-acetyl appears at 1678 cm^{-1}. In fact, the assignment is in good agreement with the expectation of the orientation during the acetylation reactions, since with hydrocarbon **1b** it is impossible to discriminate between the directing effects of the methyl and m-tolyl

substituents, because the 4-position is ortho to the methyl and para to the m-tolyl, and therefore the acetylation will occur at the 4-position as in **2b**, **3b** and **4b**. The second alternative orientation will occur at the 6′-position by the effects of the para methyl and ortho m-tolyl as in **4b**.

For compounds **2a** and **3a** (series **a**, Fig. 1) the δCH_3 of the 2-methyl and 2′-methyl is largely affected by the conformation of ring A and B. It is assumed [13], that the dihedral angle between ring A and B in biphenyl systems is $26 \pm 5^\circ$. In compound **1a** this angle becomes [16] 70.5° or close to perpendicular [4]. This explains the values of 2.12 and 2.11 ppm obtained for the 2-methyl (ring A) in **2a** and **3a** respectively, and it is anticipated that the dihedral angle in **3a** is nearly perpendicular. As a result, the δCH_3 of the 2-methyl moves to a high field relative to **1a**. The shift can be ascribed to both the ring current of ring B and steric effects of the substituents at the 2- and 2′-position. It is clear that the acetyl group is no longer ortho to the methyl group, i.e., at the 5-position in **2a** and at the 5- and 5′-position in **3a**. For compounds **2a** and **3a**, similarly **4b**, **2c** and **4c** the position of substitution could be confirmed from the UV-spectra [15] and dynamic study [19]. It was possible to determine the dihedral angle between rings A and B from the UV-spectra [17], θ could be determined from the extinction coefficient of compound **1c** (ε_0) and the compound under study (ε):

$$\frac{\varepsilon}{\varepsilon_0} = \cos^2\theta.$$

The value obtained for **1a** is 11,000 giving θ as 73°, while the ε for **2a** in chloroform solution is 12,600 with calculated θ as 68°. This value is a good support of the assignment made using ^{1}H-NMR data. This result confirms the claim that derivatives of **1a** failed to show a conjugation band of biphenyl systems in the near ultraviolet region [15] (as a result of the steric interference of the two methyl groups, which forced the benzene nuclei into a non-planar arrangement) and this will exclude any inter-ring mesomeric stabilization of a σ-complex leading to 4- (or 4′-) and 6- (or 6′-) acetylation. It is interesting to note that the carbonyl stretching for the 5- or 5′-position is 1976 cm^{-1}, indicating a non-sterically hindered carbonyl group.

4. Conclusion

The following generalization can be made from the study by proton magnetic resonance spectroscopy of mono- and diacetyl-sym-dimethylbiphenyls. For the ortho acetylation, this will shift the aromatic methyl protons to downfield, while for meta or para acetylation relative to the aromatic methyl group this will have little or insignificant variations in the aromatic methyl proton chemical shifts.

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