^{13}C NMR Spectra of Anhydrodisalicylaldehyde and related Dimers

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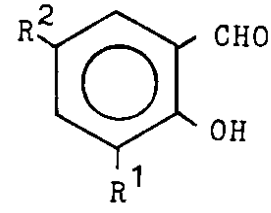
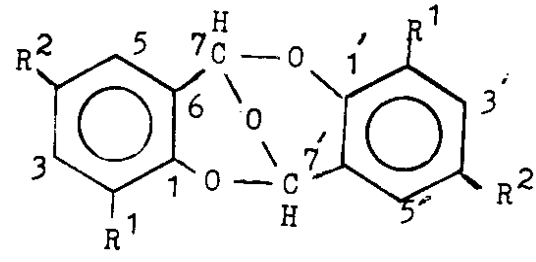
In connection with our studies on the dehydrative cyclization of o-hydroxyacetophenones using thionyl chloride, we tried first the reaction with various aldehydes such as salicyladehyde (1), o-vanillin (3) and 3-bromosalicylaldehyde (2). Anhydrodisalicylaldehyde (4), anhydrodi-o-vanillin (6) and anhydrobis (5-bromosalicylaldehyde) (5) were easily obtained from the reactions. The dimers (4) and (5) have already been described in the literature, prepared from the corresponding aldehyde with a number of dehydrating agents [1]. We report herein the ^{13}C NMR spectra of these dimers (Table 1). As is to be expected, all the dimers are symmetrical. The ^{13}C NMR spectrum of (4) showed all of the 7 expected signals from which the low field and the high field signals were assigned to carbon atoms No.1 and 7, respectively. The other ^{13}C NMR signals in the spectrum were assigned by means of single frequency off-resonance decoupling techniques by applications of known chemical rules [2]. The chemical shift of carbon No.6 in compounds (5) and (6) remains nearly in the same region as the same carbon in compound (4) and this is expected from the additivity of meta-substitution by bromide and methoxy groups [2].

Experimental

Melting points were taken on Weygand Microscopic Hot-plate apparatus and are corrected. Ultraviolet and IR spectra were measured on Unicam SP 800 and a Perkin Elmer 221 spectrometers, respectively. NMR spectra were recorded employing a Jeol FX 100 spectrometer in $CDCl_3$ containing 1% TMS Chemical shifts are expressed



1: $R^1=R^2=H$
2: $R^1=H$, $R^2=Br$
3: $R^1=OMe$, $R^2=H$



4: $R^1 = R^2 = H$
5: $R^1 = H$, $R^2=Br$
6: $R^1 = OMe$, $R^2=H$

in ppm (δ).

General method for Aldehyde Cyclization.

A mixture of thionyl chloride (2 mole) and the appropriate aldehyde

(1 mole) was kept at room temperature for 2-3 days. Then the excess of thionyl chloride was evaporated in vaccuo and the residue was recrystallized in the appropriate solvent. However, in the case of 3-bromosalicylaldehyde the mixture was refluxed for 1 hour before evaporation of the excess of thionyl chloride.

Compound (4)

MP 124°C (chloroform and pet. ether); UV ($CHCl_3$): λ_{max} 274 (4248), 282 (3570); IR (KBr): 3025, 1610, 1588, 1485, 1455, 1265, 1215, 1110, 1060, 950, 840, 800, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) : δ6.32 (2H, s) and 6.8-7.3 (8H,m); ^{13}C NMR see Table 1; Mass spectrum m/z 226 (M^+), 197, 181, 120 and 92.

Compound (5)

MP 95 °C (chloroform and pet.ether) IR (KBr): 2990, 1605, 1578, 1450, 1410, 1260, 1185, 1130, 1070, 980, 955, 855, 820, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) : δ 6.26 (2H, s), 6.76 and 7.34 (4H, AB pairs, J=8.5 Hz), 7.38 (2H, s); ^{13}C NMR: see Table 1.

Compound (6)

MP 238°C (CH_2Cl_2): UV ($CHCl_3$): λ_{max} 280, (4060); IR (KBr): 3050, 3000, 2980, 2940, 1590, 1490, 1460, 1440, 1315, 1270, 1240, 1140, 1100, 1055, 955, 815, 805, 780, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.82 (6H, 2 OMe), 6.43 (2H, s), 6.7-6.98 (6H, m); ^{13}C NMR: see Table 1.

Table-1: ^{13}C Chemical Shifts of Compound (4)-(6) in $CDCl_3$

Carbon No.	(4)	(5)	(6)
1,1	150.53 (s)	149.403(s)	140.02
2,2	116.53 (d)	118.56 (d)	147.77
3,3	127.40 (d)	134.10 (d)	112.6
4,4	121.41 (d)	113.83 (s)	119.23
5,5	130.86 (d)	130.059(d)	121.23•
6,6	119.94 (s)	121.28 (s)	120.41
7,7	90.179(d)	89.37 (d)	90.00
			56.00 (OMe)

References

1. T.Tamaki and Z.Endo, *J.Chem.Soc.Japan*, ***61***, *231 (1940)*
2. G.C.Levy, R.L.Lichter and G.L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Speectroscopy", Wiley Interscience, New York (1980); J.B.Stothers, Carbon-13 NMR Spectroscopy", Academic Press, New York (1972).