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INFLUENCE OF SUBSTITUENTS ON CARBONYL CARBON CHEMICAL SHIFTS IN 4-SUBSTITUTED BORNANE-2,3-DIONES AND THE PREPARATION OF BORNANE-2,3-DIONE

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Abstract—^{13}C Chemical shifts of the 4-substituted bornane-2,3-diones (**1–6**) have been assigned. The shielding of the CO carbons brought about by electron withdrawing substituents is attributed to a field effect of the substituent which serves to increase the CO bond order. For the substituent bearing carbons C(4), enhanced shielding is noted and these carbons exhibit small substituent chemical shifts. A preparative method leading to bornane-2,3-dione is described and briefly discussed.

Fused ring systems which are conformationally rigid are attractive substrates for the investigation of substituent effects in ^{13}C NMR spectroscopy. The extent of ^{13}C shielding and homo and heteronuclear coupling is a sensitive function of both the electronic and geometrical environment of molecules.[1–5] The carbon shielding and in particular its dependence on various structural parameters is not well understood with the consequence that in many cases unknown chemical shifts can not be predicted with meaningful accuracy. Accordingly experimental data have been collated to provide a number of empirical relationships for the estimation of chemical shifts.

There has been relatively little interest in the substituent chemical shifts (SCS) of CO carbons in systems carrying electron withdrawing substituents.[6–9] In the present study we make an extension to the 4-substituted bornane-2,3-diones (**1–6**) which contain the α-diketone moiety in an essentially rigid carbocyclic framework.[10]

RESULTS AND DISCUSSION

Assignment of the ^{13}C NMR spectra of compounds (**1–6**), given in Table 1, was assisted by proton off-resonance decoupled spectra together with extrapolation of substituent effects from related compounds.

The chemical shifts of the low field CO carbons independently show reasonable correlation with the linear free energy parameter σ_I,[11] however we were limited to six compounds on synthetic grounds.

The more deshielded CO carbon is assigned to C(2) on the basis of both the greater deshielding experienced by the CO carbon in 4-substituted bornanones[8] with respect to the 1-substituted camphenilones[9] and the more attenuated response to substituent variation.

The high field S.C.S. shown by both CO carbons C(2), C(3) in **1–6** conform to the observed pattern that electron withdrawing substituents always cause deshielding of a CO carbon.

Rationalisation of this behaviour is provided by the substituent induced variation of the CO stretching frequencies in both of the model systems, 1-substituted camphenilones and 4-substituted bornanones, in addition to the bornane-2,3-diones (**1–6**); the data are given in Table 2. In all these cases electron withdrawing substituents cause a shift of this mass-insensitive vibration[12] to higher energy; this is associated with an increased force constant for the vibration which in turn is associated with an increased bond order brought about by a movement of electrons from oxygen. The similar response of the chemical shifts of both CO carbons of **1–6** to substituent variation indicates that the substituent exerts a field effect which acts independently at C(2) and C(3). A substituent inductive effect alone if transmitted through bonds with the attenuating charge alternation pattern originally proposed for saturated hydrocarbon systems,[13] and for which manifestation has been claimed *inter alia* in the S.C.S of 1-substituted butadienes,[14] would lead to S.C.S in mutually opposing senses for the carbonyl carbons of bornanones (**1–6**).

Previously we have shown that the S.C.S of the

Table 1. ^{13}C Chemical shifts (ppm) of 4-substituted bornan-2,3-diones

Substituent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	σ_I[11]
H	58.73	204.69	202.69	58.21	22.34	30.09	42.61	21.05	17.46	8.75		0
Me	58.74	205.03	205.03	58.73	29.59	29.59	44.39	19.05	14.75	9.33	9.33	-0.05
Cl	58.46	200.11	195.56	79.09	31.34	29.03	46.99	18.36	14.88	9.81		0.47
Br	58.65	199.44	195.19	73.85	32.52	29.75	47.36	19.11	15.88	9.94		0.45
CO_2H	59.14	201.81	195.62	67.93	26.07	28.66	46.56	19.90	15.81	9.10	173.40	0.30
NO_2	59.98	198.34	189.14	99.78	26.47	27.26	47.54	18.81	14.82	9.42		0.63

Table 2. IR stretching frequencies (cm^{-1}) in Series A–D

Substituent	A	B	C	D
H	1761, 1778(sh)	1745	1745	3054
Me	1761, 1774(sh)	1745	1743	3052
NH_2		1748	1747	3051
OH		1751	1767	3053
CO_2H	1762, 1778(sh)	1753	1768	
Br	1767, 1791(sh)	1754		
Cl	1766, 1790(sh)	1759	1769	3058
NO_2	1767, 1790(sh)	1760	1771	3064

Spectra determined for dilute solutions in CCl_4: sh = shoulder

Series A = 4 Substituted Bornan-2,3-diones (this work)

Series B = 4-Substituted Bornanones (ref. 8)

Series C = 1-Substituted Camphenilones (ref. 9)

Series D = 4-Substituted Tricyclenes (ref. 14)

equivalent tertiary γ carbons C(2) and C(6) of 4-substituted tricyclenes correlated well with σ_I;[15] interestingly electron withdrawing substituents again brought about both high field shifts and also (Table 2) high energy shifts in the stretching frequency of the cyclopropyl C(2)–H bond.

In the yellow bornane-2,3-diones, $n \rightarrow \pi^*$, ν_{max} *ca.* 460 nm,[16] the absorption maximum reflects a transition lower in energy than in the corresponding monoketones, and thus more closely identified with ΔE, the mean excitation energy of the closure approximation in the paramagnetic shielding equation.[17] However the expected greater deshielding does not obtain particularly in the case of the carbonyl carbons of **1**–**6**; rather a net shielding is obtained for these carbons, attributable to greater electron density on carbon. In accord with this we have calculated that in the model systems formaldehyde and CO eclipsed glyoxal, the charge densities on carbon are 0.3285 and −0.0252 respectively.

The C(4) substituent bearing carbons in the 4-substituted bornan-2,3-diones (**1**–**6**) are the most deshielded yet observed for tertiary aliphatic carbons. This facet has been commented on previously[18] and we concur with the statement that strain plays no direct part in determining α shifts.[19]

It is noteworthy that the α-shift for C(4) in 4-bromobornan-2,3-dione is 15.7 ppm as compared with a corresponding value of 35.7 ppm in 1-bromoadamantane,[20] with intervening values for related tertiary bridgehead systems;[8,9,21] accordingly extrapolation of known α shifts for assignment purposes to related systems should be made with due caution.

We have also uncovered a route to bornane-2,3-dione from the selenium derivative **7**, itself derived from the enolate of bornanone with the aryl selenyl bromide.[22] When **7** was treated with a modest excess of hydrogen peroxide under mild conditions it was possible to isolate a *ca.* 65% yield of bornan-2,3-dione. With greater excess of hydrogen peroxide and no cooling the sole product isolated was camphoric anhydride, which was also formed on exposure of bornan-2,3-dione to the oxidation conditions.

These reactions were carried out initially in order to determine whether it was possible to extend the facile low temperature 1,2 *syn* elimination of selenoxides,[22a,23,24] where the carbon β to selenium carries a hydrogen, to a 1,3 elimination; in such a case the substrate **7** would lead to tricyclanone with retention of configuration[25] at C(3). In the event we were unsuccessful, however the results confirm organoselenium intermediates as credible intermediates in the formation of α-diketones.[22a,26] Two such immediate diketone precursors (**8**[22a] and **9**)[26] have been proposed; presently **8**, arrived at by sequential oxidation and elimination of **7**, is considered operative and the 1,3 *syn* elimination reaction is excluded, at least under these conditions.

EXPERIMENTAL

M.ps were determined on a Kofler hot-stage apparatus and are uncorrected. Microanalytical determinations were carried out in the Microanalytical Department, University of Glasgow. UV and IR spectra were recorded on Unicam Sp 8000 and Beckmann 225 instruments respectively. ^{13}C NMR spectra were recorded on a Varian XL 100 spectrometer operating in the Fourier transform mode at 25.2 MHz. Proton noise decoupling was effected by a broad band decoupler. Probe temp. was 35° and chemical shifts (ppm from internal TMS) are accurate to 0.05 ppm; spectra were determined on 0.3 M solns of substrate in $CDCl_3$.

The bornan-2,3-diones were prepared by the method of Evans *et al.*[27] Modifications of the temp. and reaction time were necessary in order to optimise yields in the cases of **3**–**6**; the appropriate conditions for **3**–**5** were 110°, 8 days and for **6** 105–110°, 14 days. Pure samples were obtained by recrystallisation from EtOAc.

4-*Methylbornan*-2,3-*dione* (**2**) had m.p. 198–200° rather than the value quoted by us previously.[8]

4-*Chlorobornan*-2,3-*dione* (**3**) had m.p. 219–221° (lit.[28] 219–220°), λ_{max} 457 nm (ϵ 37.0) (Found: C, 59.84; H, 6.53. Calc. for $C_{10}H_{13}ClO_2$: C, 59.67; H, 6.59%).

4-*Bromobornan*-2,3-*dione* (**4**) had m.p. 227–9°, λ_{max} 456 nm (ϵ 49.8) (Found: C, 49.00; H, 5.34. Calc. for $C_{10}H_{13}BrO_2$: C, 49.19; H, 5.53%).

Bornan-2,3-*dione*-4-*carboxylic acid* (**5**) had m.p. 251–3°, λ_{max} 459 nm (ϵ 27.8) (found: C, 62.70; H, 6.90. Calc. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71%).

4-*Nitrobornan*-2,3-*dione* (**6**) had m.p. 209–11°. (Found: C, 56.50; H, 5.95; N, 6.91. Calc. for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20;

N, 6.23%). This material is rather unstable and decomposes both on standing and on tlc plates (e.g. Merck silica). Additionally, some attempts at preparation of **6** were unsuccessful.

endo - 3 - (p - *t* - *Butylphenylselenobornanone* (**7**). To a stirred soln of bornanone (2.3 g, 1.5×10^{-2} mol) in THF (20 ml, freshly distilled from lithium aluminium hydride) was added n-BuLi (15%, 8 ml Fluka) under N_2 and the soln stirred under N_2 at 0° for 30 min.[29] To a soln of di-(*p*-t-butylselenide)[30] (3.8 g, 9×10^{-3} mol) in dry THF (10 ml) in a pressure equalising dropping funnel was added Br_2 (1.6 g, 1.0×10^{-2} mol) dropwise and the soln agitated[22a] until it was homogeneous. This soln was rapidly added to the cold enolate soln under N_2 and with stirring. After 8 hr the resultant soln was added to dil HCl and ether/pentane (1:1) soln. The organic layer was washed with water, $NaHCO_3$ aq, brine and dried (Na_2SO_4). Evaporation of the solvent after filtration gave an *oil* (5.2 g), which after column chromatography on neutral alumina and recrystallisation from cyclohexane gave **7** (1.84 g, 34%). M.p. 85–6°; ν_{max} (CCl_4) 3035, 1745 cm^{-1}, NMR ($CDCl_3$) 0.89; 0.95; 1.01 (all 3H, s); 1.30 (9H, s); 2.4–1.4 (5H, m); 4.25 (1H, d, J = 4.5 Hz); 7.67, 7.58, 7.35, 7.25 (4H, AA^1BB^1 pattern, aromatic protons). (Found: C, 66.4; H, 7.5. Calc. for $C_{20}H_{28}SeO$ requires: C, 66.1; H, 7.7%).

Reaction of **7** *with excess hydrogen peroxide*. To a stirred soln of **7** (1.7 g, 4.7 mmol) in CH_2Cl_2 (4 ml) was added a 4-fold molar excess of 30% H_2O_2. An exothermic reaction soon set in and was moderated by immersion in ice-water. After 15 min the organic layer was separated, washed successively with water and brine and dried (Na_2SO_4). After filtration and removal of solvent there remained a white solid (0.7 g) which was identical with a commercial sample (B.D.H.) of camphoric anhydride.

Reaction of **7** *with hydrogen peroxide*. To a stirred solution of **7** (1.7 g, 4.7 mmol) in CH_2Cl_2 (6 ml) at 0° was added 1.1 mmol of 30% H_2O_2. After 10 min the yellow soln was worked up as above to give after recrystallisation (EtOAc) bornane-2,3-dione, identical with a sample prepared by a literature method,[27] in 65% yield. Examination of the mother liquors by tlc indicated the absence of both tricyclanone and camphoric anhydride.

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