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THE ULTRAVIOLET ABSORPTION SPECTRA, AND THE CYANOHYDRIN EQUILIBRIA OF SOME ACETYL DERIVATIVES OF ARYL ETHERS AND THIOETHERS

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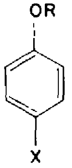
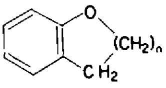
Abstract—The equilibrium constants for the reaction: ketone + HCN $\rightleftharpoons$ cyanohydrin, are reported for the ketones Ib and IIIb (R = Me, Et, Pr^i), Ib (R = Bu^t) and IVb (n = 1, 2 and 3). The data for the equilibria reveal a progressive decrease in the stability of the ketone (relative to its cyanohydrin) in the order: Me > Et > Pr^i > Bu^t, and n = 1 > 2 > 3. This is attributed to increased steric interactions between R and an *o*-hydrogen atom in Ib and IIIb, and in the saturated hetero-ring in IVb. The same type of steric interaction is believed to operate in the spectroscopically excited states of Ib, where it opposes the stabilizing inductive effect of R, thus causing the observed trends in the spectra.

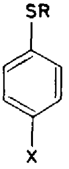
During the last two decades, much evidence has been assembled which shows that the mesomeric interaction between an aromatic nucleus and a substituent possessing either a multiple linkage or a lone pair of electrons, is subject to restriction by steric interactions. The effects of the interplay of these factors upon the chemical and the physical properties of such molecules are diverse, and they have been reviewed by Wepster.[1]



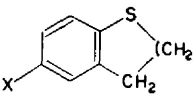
Ia: X = H
b: X = Ac



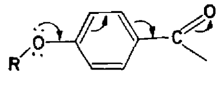
II



III a: X = H
b: X = Ac



IV a: X = H
b: X = Ac



V

Baddeley *et al.* have shown[2] that with aromatic ethers of the types Ia (R = Me, Et, Pr^1 and Bu^t, respectively) and II (n = 1 – 3), steric interactions, involving either R and the *o*-hydrogen atom in Ia or the C—H linkages of the hetero-ring in IIa, modify the degree of (electron-releasing) mesomerism between the oxygen atom and benzene ring. More recently, we have shown[3] that for the analogous thioethers, IIIa (R = Me, Et, Pr^1 and Bu^t, respectively) and IVa (n = 1 – 3), and their acetyl derivatives, IIIb (R = Me, Et, and Pr^1) and IVb (n = 1 – 3), respectively, mesomeric interaction involving the sulphur atom and benzene ring is similarly affected by steric influences. We now report the equilibrium constants for the dissociation of

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[1] B. M. Wepster, *Progress in Stereochemistry* (Edited by Klyne and de la Mare) Vol. 2; p. 99. Butterworth (1958).

[2] G. Baddeley, N. H. P. Smith and M. A. Vickars, *J. Chem. Soc.* 2455 (1956).

[3] M. J. Y. Foley and N. H. P. Smith, *J. Chem. Soc.* 1899 (1963).

the cyanohydrins of the ketones, Ib (R = Me, Et, Pt^{i} and Bu^{t}, respectively), IIIb (R = Me, Et and Pr$_{i}$, respectively) and IVb (n = 1 — 3, respectively), together with the UV absorption spectra of Ib (R = Me — Bu^{t}, respectively). The dissociation constants are given in Table 1, and the light absorption data in Table 2.

For the series of compounds Ib and IIIb, the data confirm the findings of Baker, *et al.*,[5] namely, that in the *para*-position, both oxygen and sulphur release electrons towards the benzene ring, the order of magnitude of this (mesomeric) interaction being O > S. Moreover, within the two series of compounds, variation of R produces parallel trends in the values of K: Me > Et > Pr^{i} (> Bu^{t}, for Ib). Since increase in the value of K denotes increased stability of the ketone relative to its cyanohydrin, this trend is indicative of a decrease in the stability of the ketone, doubtless as a

Table 1. Equilibrium constants, $K(= k_2/k_1)$, for the reaction: $Ar.CO.Me + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ar.CMe(OH)CN$, in constant-boiling ethanol at 20°

Ketone	K (mole l^{-1})	ΔG (cals)
Ib; R = Me	6·82	−1119
R = Et	3·73	− 768
R = Pr^{i}	3·14	− 667
R = Bu^{t}	3·04	− 649
IIIb; R = Me	2·95	− 631
R = Et	2·85	− 611
R = Pr^{i}	2·04	− 416
IVb; n = 1	4·56	− 855
n = 2	3·17	− 673
n = 3	1·95	− 389
Ph.CO.Me*	1·33	− 166

* Lapworth and Manske[4] give K = 1·30

Table 2. Ultraviolet absorption spectra in hexane of p-alkoxy- and p-alkylthioacetophenones, (Ib and IIIb)

	Ib		IIIb*	
Substituent, R.	λ_{max}(Å)	ε_{max}	λ_{max}(Å)	ε_{max}
Me	2635	17,850	2950	18,600
			3040	19,900
Et	2645	18,650	2970	16,600
			3050	17,280
Pr^{i}	2660	18,100	3010	15,990
			3080	16,750
Bu^{t}	2560	13,990	—	—

* Data from Foley and Smith[8]

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[4] A. Lapworth and R. Manske, *J. Chem. Soc.* 1976 (1930).

[5] J. W. Baker, G. F. C. Barrett and W. T. Tweed, *J. Chem. Soc.* 2831 (1952).

consequence of the increasing steric interaction between R and an *o*-hydrogen atom. As expected, the imposition of coplanarity between the sulphide group and the benzene ring increases the stability of the ketone containing the five-membered ring (IVb; n = 1). As the hetero-ring is enlarged (n = 1 to 2 to 3), these ketones suffer a progressive decrease in stability. This is presumably due to the steric requirements of the saturated hetero-ring rotating the S—CH_2 bond out of the plane of the aromatic ring, in order that the former may assume its most stable conformation.

The ketones (Ib) possess two regions of absorption in the ultraviolet, at approximately 2150 and 2600 Å, respectively. In the former region, not all the compounds of the series give absorption maxima; of those compounds which do, there is no obvious regularity in the changes in λ and ε, caused by changes in R. The absorption characteristics in this region of the spectrum will therefore not be considered further. Unlike the corresponding sulphur analogues (IIIb; Table 2), the compounds (Ib) possess only a single absorption peak in the region 2600 Å. For the reasons given previously,[3] we identify this band as a *K*-band (cf. Burawoy[6]), which most probably arises from transitions of the type V. The trend in λ, (Me $<$ Et $<$ Pr^i) $>$ Bu^t, is substantially the same as that observed for the corresponding sulphur compounds, (IIIb; R = Me — Pr^i), and it may be accounted for on the basis of the operation of two opposing factors which affect the stability of the excited state, namely, stabilization by inductive electron-release from R, and destabilization by steric interaction between R and an adjacent hydrogen atom, the magnitudes of both of these interactions increasing in the order, Me $<$ Et $<$ Pr^i $<$ Bu^t.

EXPERIMENTAL

Materials. The ketones IIIb and IVb were described previously.[3]

p-*Methoxyacetophenone*,[7] b.p. 130°/10 mm, m.p. 37–38° (from light petroleum, b.p. 0–40°) was obtained by the methylation of *p*-hydroxyacetophenone with dimethyl sulphate in the presence of alkali.

p-*Ethoxyacetophenone*,[8] b.p. 139°/15 mm, m.p. 36–37° (from light petroleum, b.p. 0–40°) was obtained from ethyl phenyl ether by Friedel-Crafts acetylation, using Baddeley's modification.[9] The semicarbazone[10] separated from acetone as needles, m.p. 184–185° (Found: N, 19·1. Calc. for $C_{11}H_{15}N_3O_2$: N, 19·0%).

p-*Isopropoxyacetophenone*, b.p. 152°/18 mm, m.p. 38–39° (from light petroleum, b.p. 0–40°), was prepared from *p*-hydroxyacetophenone and isopropyl bromide by Bradley and Robinson's procedure.[11] Its *semicarbazone* had m.p. 186–187° (from acetone) (Found: N, 17·8. $C_{12}H_{17}N_3O_2$ requires: N, 17·9%).

p-*t-Butoxyacetophenone*. A solution of methyl magnesium iodide [prepared from methyl iodide (16·4 g) and magnesium (2·8 g)] in ether (75 ml) was treated with a solution of *p*-t-butoxybenzonitrile[3] (18·4 g) in anhydrous benzene (75 ml). The mixture was heated under reflux for 45 min, and then allowed to stand at room temp for 16 hr. Decomposition with glacial acetic acid (20 ml) and ice-water (100 ml) followed, and after the usual isolation procedures, distillation gave a colourless, refractive oil (16·8 g), b.p. 80–81°/0·2 mm, n_D^{18} 1·5223 (Found: C, 75·2; H, 8·6. $C_{12}H_{16}O_2$ requires: C, 75·0; H, 8·3%). The *semicarbazone* had m.p. 198–198·5° from aqueous ethanol. (Found: C, 62·7; H, 7·5; N, 16·6. $C_{13}H_{19}N_3O_2$ requires: C, 62·6; H, 7·6; N, 16·9%).

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[6] A. Burawoy, *J. Chem Soc.* 1177 (1939); *Tetrahedron* **2,** 122 (1958).

[7] F. G. Pope, *Proc. Chem. Soc.* **28,** 332 (1912).

[8] L. Gattermann, R. Ehrhardt and H. Maisch, *Ber. Dtsch. Chem. Ges.* **23,** 1205 (1890).

[9] G. Baddeley, *J. Chem. Soc.* S99 (1949).

[10] F. Unger, *Liebigs Ann.* **504,** 267 (1933).

[11] W. Bradley and R. Robinson, *J. Chem. Soc.* 2362 (1926).

Determination of equilibrium constants. The method of Baker and Hemming,[12a] as modified by Baker *et al.*[12b] was used. For each compound, the mean of at least three determinations agreeing to within 5% was taken.

Ultraviolet absorption spectra. These were determined in hexane solution using a Hilger Uvispek instrument.

Acknowledgement—We thank Mr. B. Manohin and his staff for the analyses.

[12a] J. W. Baker and M. L. Hemming, *J. Chem. Soc.* 191 (1942).
[b] J. W. Baker, J. A. L. Brieux and D. G. Saunders, *J. Chem. Soc.* 404 (1956).