# **853.** *4-t-Butylthioacetophenone: its Ultraviolet Absorption Spectrum, and Cyanohydrin Dissociation Constant*

By N. H. P. SMITH

As part of a study of the effects of molecular constitution upon the physical and the chemical properties of aromatic sulphides, the ultraviolet absorption spectra[1] and the cyanohydrin dissociation constants[2] of the ketones (I; R = Me, Et, and $\mathrm{Pr^i}$, respectively) have been determined.

Attempts to prepare the t-butyl analogue (I; R = $\mathrm{Bu^t}$) by Friedel–Crafts acetylation of phenyl t-butyl sulphide[3] were fruitless.

Interaction of *p*-chloroacetophenone and 2-methylpropane-2-thiol under the conditions described in the patent specification[4] resulted in the recovery of more than 90% of the starting ketone. However, addition of pyridine to the heterogeneous mixture gave a uniform solution in which displacement of the chlorine atom by the thiolate anion occurred smoothly, forming compound (I; R = $\mathrm{Bu^t}$) in high yield.

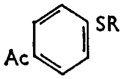
Alkylation of *p*-acetyl(thiophenol) with t-butyl alcohol in the presence of perchloric acid[5] also afforded compound (I; R = $\mathrm{Bu^t}$). The identity of these two compounds was proved by infrared spectroscopy.

Conversion of the sulphide (I; R = $\mathrm{Bu^t}$) into the sulphone, by use of 30% hydrogen peroxide in glacial acetic acid, proceeded readily in high yield and with no trace of cleavage of the $\mathrm{C_t}$–S linkage. This is consistent with observations made on the oxidation of phenyl t-butyl sulphide[6] and of other sulphides containing the t-butyl group.[7]

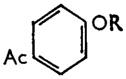
Reference to the Table shows that, relative to its cyanohydrin, the ketone (I; R = $\mathrm{Bu^t}$) is the least stable of the series (I; R = Me, Et, $\mathrm{Pr^i}$, and $\mathrm{Bu^t}$, respectively) (for the remaining data, see ref. 2). This is consistent with the trend observed[2] for the analogous alkoxy-compounds (II). Moreover, replacement of the $\mathrm{Pr^i}$ group by $\mathrm{Bu^t}$ causes a greater decrease in the stability of the alkylthio-compound (I) than it does in that of the alkoxy-analogue (II). This is a consequence of the competition between the repulsive interaction of the *ortho*-hydrogen atom and the t-butyl group, and the steric requirements for maximal conjugation of the aromatic ring with either the oxygen or the sulphur atom.[8] The latter requires the maintenance of coplanarity between the $\mathrm{C_t}$–O(S) linkage and the benzene ring,

Dissociation constants for the cyanohydrins, Ar·CMe(OH)CN, in constant-boiling ethanol at 20°

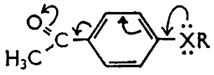
| Ketone | *K* (mole l.$^{-1}$) | Δ*G* (cal.) | Ketone | *K* (mole l.$^{-1}$) | Δ*G* (cal.) |
|---|---|---|---|---|---|
| (I; R = $\mathrm{Bu^t}$) ...... | 1·45 | −218 | (II; R = $\mathrm{Bu^t}$) ... | 3·04 | −649 |
| (I; R = $\mathrm{Pr^i}$) ...... | 2·04 | −416 | (II; R = $\mathrm{Pr^i}$) ... | 3·14 | −667 |



(I)



(II)



(III)

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[1] M. J. Y. Foley and N. H. P. Smith, *J.*, 1963, 1899.

[2] M. J. Y. Foley, N. H. P. Smith, and P. Watts, *Tetrahedron*, 1964, **20**, 1555.

[3] Cf. M. J. Y. Foley, Thesis, Manchester, 1960.

[4] U.S.P. 2,905,719/1959.

[5] M. E. Cain, M. B. Evans, and D. F. Lee, *J.*, 1962, 1694.

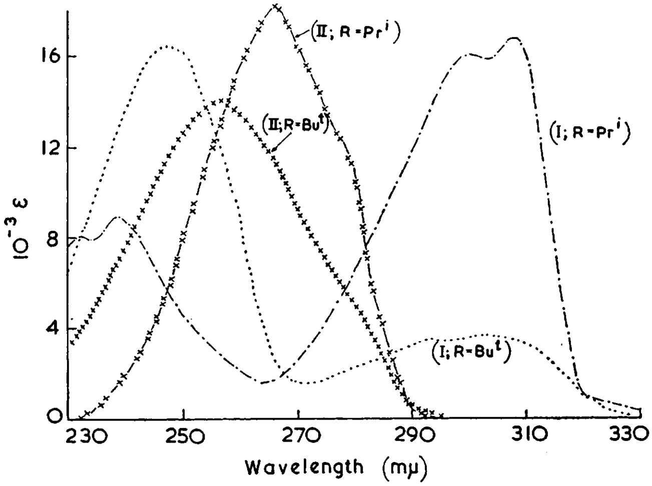
[6] V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Amer. Chem. Soc.*, 1938, **60**, 2731; E. A. Fehnel and M. Carmack, *ibid.*, 1949, **71**, 231.

[7] G. E. Bermingham, unpublished results.

[8] G. Baddeley, N. H. P. Smith, and M. A. Vickers, *J.*, 1956, 2455.

whereas the former tends to rotate this linkage out of the aromatic ring's plane. Mesomeric interaction as in formula (III) leads to greater stabilisation when X = O than when X = S. The available evidence [9] indicates that the bond angle ∠CSC is smaller than ∠COC. Consequently, greater interpenetration of the van der Waals radii of the t-butyl group and of the *ortho*-hydrogen atom will occur as the $C_t$–S linkage approaches coplanarity with the aromatic ring, than will be the case with the $C_t$–O linkage. (Indeed, Catalin models would suggest that coplanarity of the $C_t$–S bond and the aromatic ring is possible only if there is lateral distortion of the $C_a$–S bond (a = aromatic) in the plane of the benzene ring.) Hence, for the compounds (I and II; R = Bu$^t$), replacement of O by S leads to decreased mesomeric stabilisation accompanied simultaneously by increased steric congestion between the t-butyl group and the *ortho*-hydrogen atom. Overall, these effects cause a convergence in the relative free-energy levels associated with compound (I; R = Bu$^t$) and its cyanohydrin, as compared with those of compound (II; R = Bu$^t$) and its cyanohydrin.

The Figure reproduces the ultraviolet absorption spectra in hexane of compounds (I; R = Pr$^i$ and Bu$^t$) and of compounds (II; R = Pr$^i$ and Bu$^t$). The hypsochromic shift and simultaneous decrease in ε of the long wavelength band of compound (I), as R changes from Pr$^i$ to Bu$^t$, is as expected. Noteworthy is the decrease in ε for each t-butyl compound, relative to the value of ε for the isopropyl analogue. These observations lend support to the view that the spectroscopically excited state for compound (I; R = Bu$^t$) is considerably less stabilised than is that for compound (II; R = Bu$^t$), and is therefore much more sensitive to strong steric interactions.



*Experimental.*—4-(*t-Butylthio*)*acetophenone*. (*a*) A solution of 4-chloroacetophenone (31 g.), 2-methylpropane-2-thiol (18 g.), and sodium hydroxide (8 g.) in water (50 ml.) and pyridine (90 ml.) was heated at 200° for 3 hr. in a steel bomb. When cool, the organic material was extracted into ether, from which solution the pyridine was removed with dilute acid. After drying of the neutral solution followed by removal of the solvent, distillation of the residue gave material, b. p. 79—109°/0·2 mm.; redistillation gave, after a small fore-run, a *fraction*, b. p. 107—108°/0·3 mm. (24·7 g.), $n_D^{17}$ 1·5561 (Found: C, 69·0; H, 7·8; S, 15·3%; *M*, 215. $C_{12}H_{16}OS$ requires C, 69·2; H, 7·7; S, 15·4%; *M*, 208). The *semicarbazone* separated from aqueous ethanol as needles, m. p. 220—221° (Found: C, 58·7; H, 7·3; N, 16·0. $C_{13}H_{19}N_3OS$ requires C, 58·9; H, 7·2; N, 15·9%).

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[9] "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, 1958.

(*b*) 4-Aminoacetophenone (22·5 g.) was converted [3] into 4-acetyl(thiophenol), the xanthate method being used. Without further purification, the 4-acetyl(thiophenol) was dissolved under nitrogen in acetic acid (50 ml.) containing t-butyl alcohol (12·3 g.). To this was added a solution in glacial acetic acid (50 ml.), through which nitrogen gas had previously been passed, of acetic anhydride (18·5 g.) and 72% perchloric acid (11·6 g.). The combined solution was kept at 30° for 24 hr.[5] The mixture was poured into brine, and then extracted with ether. After neutralisation of acidic material, drying, and removal of the solvent, distillation gave a small fore-run, followed by material (12·3 g.), b. p. 120—123°/4 mm., $n_D^{17}$ 1·5589 (Found: C, 69·0; H, 7·6; S, 15·3%; *M*, 208. $C_{12}H_{16}OS$ requires C, 69·2; H, 7·7; S, 15·4%; *M*, 208).

The infrared spectra of the two specimens were identical.

4-*t-Butylsulphonylacetophenone*. A solution of the above sulphide (5·2 g.) in glacial acetic acid (25 ml.) containing 30% hydrogen peroxide (15 ml.) was heated under reflux for 90 min., and was then poured into ice-water. The resulting *solid* was crystallised from light petroleum (b. p. 80—100°); needles, m. p. 108—108·5°, being obtained (Found: C, 59·7; H, 6·4; S, 13·1. $C_{12}H_{16}O_3S$ requires C, 60·0; H, 6·7; S, 13·3%).

The cyanohydrin dissociation constant, and the ultraviolet absorption spectrum, were determined as described previously.[2]

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