On the Relative Acidity of Cycloheptatriene and Toluene

A. Walter Zwaard* and Hendrik Kloosterziel*

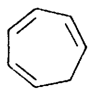
Department of Organic Chemistry, Gorlaeus Laboratories, P.O. Box 9502, University, 2300 RA Leiden, The Netherlands

The proton of the cycloheptatrienyl moiety in 7-benzylsulphonyl-1,3,5-cycloheptatriene is found to be at least 300 times more acidic than those of the benzyl moiety in the same molecule towards potassium amide in liquid ammonia (at −40 °C).

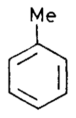
The occurrence of the unsubstituted 8π (anti-aromatic) cycloheptatrienyl anion $C_7H_7^-$ was first demonstrated by Dauben and Rifi,[1] who concluded from competition experiments that cycloheptatriene (**1**) (pK_a 36) is more acidic than its isomer toluene (**2**) (pK_a 37). The pK_a values mentioned are cited [2a] by Cram in his classical treatise, but on combining several sets of data, resulting in his well known M.S.A.D. scale, he concluded that (**1**) (pK_a 36) is less acidic than (**2**) (pK_a 35).[2b]

Previously we have shown (by ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopy) that α-sulphonyl-substituted toluenes yield stable benzylic carbanions[3] and recently that 7-sulphonyl-substituted cycloheptatrienes give stable cycloheptatrienyl anions[4,5] upon treatment with potassium amide in liquid ammonia.

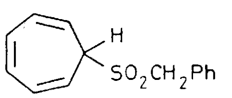
We report the result of an intramolecular deprotonation experiment. 7-Benzylsulphonylcycloheptatriene (**3**) gave exclusively the (benzylsulphonyl)cycloheptatrienyl anion {^{1}H n.m.r.: δ 7.3 [5H, s(br), C_6H_5], 3.47 (2H, d, *J* 11.5 Hz), 3.29 (2H, s, CH_2), 3.09 (2H, m), and 2.12 (2H, m); the coupling constants in the multiplets are similar to those of other substituted cycloheptatrienyl carbanions[4,5]}. The proton-decoupled ^{13}C n.m.r. spectrum is also in accordance with the cycloheptatrienyl structure and is shown in Figure 1. Besides



(**1**)



(**2**)



(**3**)

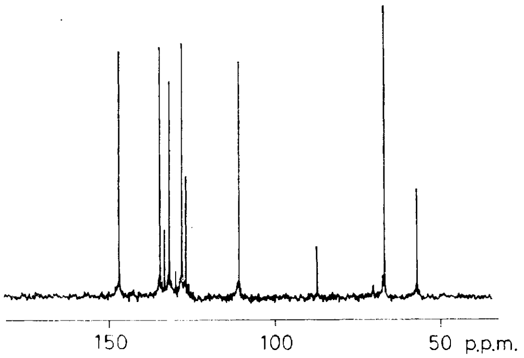


Figure 1. Proton-decoupled ^{13}C n.m.r. spectrum of (**3**), treated with one equivalent of potassium amide in liquid ammonia at −40 °C.

the reference signal of dioxan (at 67.1 p.p.m.) nine signals can be observed. Four of these (147.3, 135.0, 111.1, and 87.6 p.p.m.) are readily assigned to carbon atoms of the seven-membered ring by comparison with the ^{13}C n.m.r. spectra of solutions of cycloheptatrienyl anions.[5] The four remaining low-field resonances (at 133.6, 132.1, 128.4, and 127.1 p.p.m.) pertain to the phenyl carbon atoms. The signal at 57.2 p.p.m. becomes a triplet in a gated-decoupled ^{13}C n.m.r. spectrum and thus belongs to the (unionized) CH_2 group.[†] Knowing where the signals of the benzylic anion are likely to occur, we estimate its presence to be at most 2%. Applying a statistical factor of 2 we conclude that the proton of the cycloheptatrienyl moiety of **(3)** is at least 100 times more acidic than those of the benzyl moiety.

Upon introducing a *p*-chloro substituent into **(3)** these results are not changed. With an approach similar to a Hammett relation and using the σ-value for the *p*-chloro substituent (+0.23) and a ρ-value of at least 2 for the ionization constant of the substituted compounds **(3)**[‡] at −40 °C in liquid ammonia it follows that the ratio of 100:1 should be raised by at least a factor of three.[§]

Part of this work was supported by The Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from The Netherlands Organisation for the Advancement of Pure Research (Z.W.O.).

Received, 29th December 1981; Com. 1471

References

1 H. J. Dauben and M. H. Rifi, *J. Am. Chem. Soc.*, 1963, **85**, 3042.
2 D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1963, (a) p. 15, (b) p. 19.
3 E. A. Zonneveld and H. Kloosterziel, unpublished results.
4 A. W. Zwaard and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 126.
5 A. W. Zwaard, thesis to be published.

[†] A related phenomenon of interest is the fact that an equimolar mixture of 7-methoxycarbonylcycloheptatriene and methylphenylacetate, when treated with one mol. equiv. of potassium amide in liquid ammonia at −40 °C, results in the formation of the methoxycarbonylcycloheptatriene anion (identical with that reported in ref. 4) and no observable formation of the benzylic anion.

[‡] ρ for the ionization of phenols is 2.1 (25 °C, H_2O; H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191), of anilines 5.3 (31 °C, NH_3; T. Birchall and W. L. Jolly, *J. Am. Chem. Soc.*, 1966, **88**, 5439), and of toluenes 12 (25 °C, dimethyl sulphoxide; F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, 1977, **42**, 1817).

[§] However, when **(3)** is treated with a small (catalytic) amount of KNH_2 in ND_3 both the seven-membered ring proton and the benzylic protons are completely exchanged by deuterium at −40 °C (according to ^1H n.m.r. spectroscopy) within the time necessary to record the n.m.r. spectrum.