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A NEUTRAL STABLE CYCLOHEPTATRIENONE-AMINE ADDUCT : A PECULIARLY STABILIZED SULFONIUM YLID

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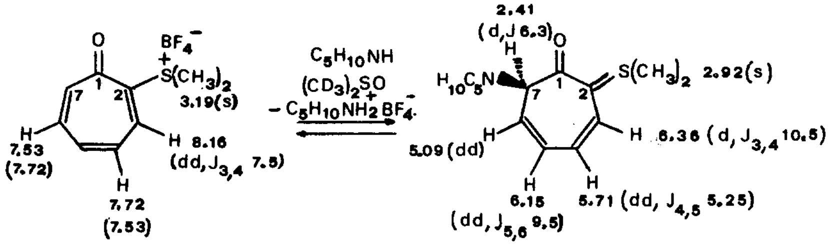
Although several anionic sigma-adducts of cycloheptatrienones and either alkoxides[1] or thiolates[2] have been characterized by ^{1}H nmr spectroscopy, evidence for similar adducts in the synthetically important reactions with amines,[3] owing to their lability and low association constants, merely rests on uv spectra and kinetics.[4]

We report the first ^{1}H nmr observation of an adduct between a cycloheptatrienone and an amine. Thus, on the addition of one drop of dried piperidine to 0.5 ml of a 0.1 M solution of the sulfonium salt 1,[†] mp 130-132°, in dried $(CD_3)_2SO$ the ^{1}H nmr signals due to 1 immediately disappeared while those attributable to 2 appeared. On neutralization the reaction was reversed.



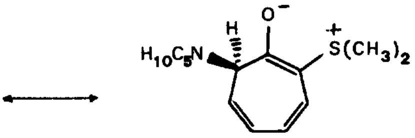
(1) (2a)

[δ values in ppm with respect to internal TMS for 1 and 2; J values in Hz]

Structural assignment of 2 is supported by the result of a similar experiment with the C_3, C_5, C_7-trideuterio analog of 1, mp 130-131°,[†] whereby two broad ^{1}H nmr singlets at δ5.09 and 5.71, besides a singlet at δ2.92 ppm, were observed. Moreover, on irradiation at δ2.92 ppm, N.O.E. at only the 6.36 ppm doublet of 2 was observed.

We favor the unusual, without charge separation, sulfonium ylid[5] form 2a, vs 2b, because no 2-piperidinotropone, which would have required protonation

(2a)



(2b)

of 2 at C_2,[4] was detectable. This is consistent with the observations that in aqueous alkali 1 gives salicylaldehyde, the aldehyde yield increasing with alkali concentration, whereas when 1 is treated with aqueous piperidine buffered with piperidinio fluoborate m-hydroxybenzaldehyde is formed. In fact, in the most likely routes to the aldehydes, 2 needs not to become protonated.[5]

FOOTNOTES

[†] Satisfactory elemental analyses were obtained. Structural assignment is supported by the N.O.E. on irradiation at δ 3.19 ppm whereby only the signal at δ 8.16 ppm was affected.

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