Preparation of Stable Quinone Methide Imines

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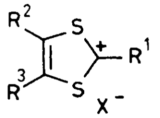
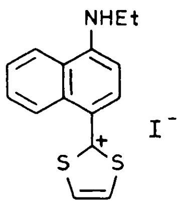
Summary Primary and secondary aromatic amines undergo electrophilic aromatic substitution with 2-methylthio-1,3-dithiolylium salts to give the corresponding 2-aryl-1,3-dithiolylium salts, which are deprotonated by 1,8-diazabicyclo[5.4.0]undec-5-ene to yield stable quinone methide imines.

THERE have been many recent reports on the syntheses of stable quinodimethanes,[1] quinone methides,[2] and thioquinone methides,[3] but only one report on the synthesis of stable quinone methide imines.[4] Quinone methide imines cannot be prepared from aromatic amines and carbonium salts by processes analogous to those that have proved valuable for the preparation of quinone methides and quinodimethanes.[4] However, we have now found that 1,3-dithiolylium salts preferentially attack the aromatic ring of primary and secondary aromatic amines rather than nitrogen when this is sterically hindered,[5] and that the resulting dithiolylium salts are deprotonated by 1,8-diazabicyclo[5.4.0]undec-5-ene (DBU) to yield stable quinone methide imines.



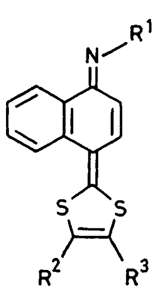
(1)



(2)

	R^1	R^2	R^4	X
a;	SMe	H	H	I
b;	SMe	–CH=CHCH=CH–		ClO_4
c;	H	–CH=CHCH=CH–		BF_4

The dithiolylium salt (**1a**) reacted with *N*-ethyl-1-naphthylamine in boiling acetonitrile to give the dithiolylium salt (**2**)† (35%), m.p. 217—218 °C. Treatment of (**2**) with DBU in acetonitrile at 0 °C yielded the stable quinone methide imine (**3a**)† (97%), orange needles (from hexane), m.p. 117 °C; δ ($CDCl_3$) 1·35 (3H, t), 3·68 (2H, q), 6·59 (1H, d), 6·60 (2H, s), 7·16 (1H, d), 7·2—7·7 (2H, m), 7·8—8·1 (1H, m), and 8·4—8·7 (1H, m). Triethylamine did not bring about this conversion. Similarly the imine (**3c**), m.p. 147 °C, was prepared from (**1b**) and *N*-ethyl-1-naphthylamine. The *N*-unsubstituted imine (**3d**), m.p. >260 °C (decomp.), was also obtained from (**1b**) and 1-naphthylamine, although the unstable imine (**3b**) could not be isolated.

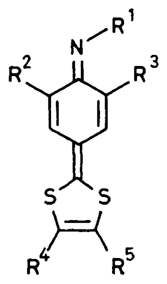


(3)

	R^1	R^2	R^3
a;	Et	H	H
b;	H	H	H
c;	Et	-CH=CHCH=CH-	
d;	H	-CH=CHCH=CH-	

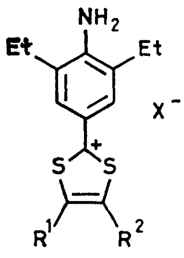
The salt (**1b**) also undergoes electrophilic aromatic substitution with *N*-s-butylaniline and this enabled the imine (**4a**) to be synthesized, m.p. 147—149 °C, which has no substituent on the quinonoid unit.

2,6-Diethylaniline and (**1a**) afforded (**5a**), which on treatment with DBU gave (**4b**) as unstable yellow crystals. The stable imine (**4c**), m.p. >220 °C (decomp.), can be prepared from (**5b**), which is itself obtained by reaction of 2,6-diethylaniline and 2 mol. equiv. of (**1c**): the initial product (**6**) is converted into (**5b**) by hydride abstraction by (**1c**).

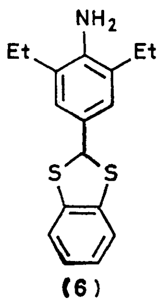


(4)

	R^1	R^2	R^3	R^4	R^5
a;	Bu^s	H	H	-CH=CHCH=CH-	
b;	H	Et	Et	H	H
c;	H	Et	Et	-CH=CHCH=CH-	



(5)



(6)

	R^1	R^2	X
a;	H	H	I
b;	-CH=CHCH=CH-		BF_4

The physical and chemical properties of the stable quinone methide imines reported here are of current interest in connection with conducting charge-transfer salts of TTF and TCNQ[6] and are also relevant to the question of aromaticity of 1,3-dithiolylium ions and related compounds.[7]

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† Satisfactory elemental analyses were obtained for all new 1,3-dithiolylium salts and stable quinone methide imines.

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