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Dispironaphthalenones and Spironaphthalenones as Novel Dehydrogenation Reagents

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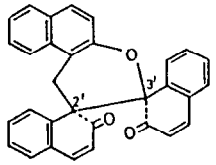
ABSTRACT: Dehydrogenation of a number of dihydroaromatic substrates has been carried out using either dispironaphthalenone 1 or spironaphthalenones 2 & 3 as dehydrogenating agents. The reaction is over in refluxing mesitylene in 1-2 hr and the yields of the aromatised products are fairly good (65-70%).

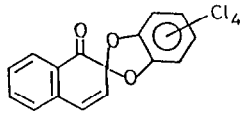
Dehydrogenation reactions are of great synthetic utility. The principal methods cited in the older literature involve the use of S,Se or the Pt group metals.[1] Although these reagents find useful applications, they require invariably drastic conditions which are not useful in the synthesis of labile compounds . High potential quinones like DDQ & o-chloranil provide milder methods of dehydrogenation as well as a method for selective removal of hydrogen from hydroaromatic compounds.[2] The disadvantage of using o-chloranil is that quinone adducts might be formed along with dehydrogenation.[3] The trityl carbocation has been used to dehydrogenate a series of hydroaromatic compounds.[4] However, it is usually difficult to separate the by product,triphenylmethane, from the aromatised product. AlkylLi-TMEDA method has also been used to dehydrogenate hydroaromatic compounds.[5]

We have been engaged in the study of reactions of spirocompounds 1,2 & 3, which could conveniently be synthesised.[6,7] The X-ray crystal structure of 1 shows that the C(2′)-C(3′) bond is unusually long (1.616A°). This bond readily cleaves homolytically under a variety of reaction conditions.

Catalytic hydrogenation and Zn/AcOH reduction cleaves this bond to give a dihydroxy compound.[6] Photolysis or pyrolysis of this compound also cleaves this bond to give the products resulting from the rearrangement of the initially formed radical intermediate.[9] It was considered that, if this radical intermediate could abstract hydrogens from hydroaromatic substrates, a new method for dehydrogenation would be available on hand. In order to check the possibility of using 1 as a dehydrogenating agent, a number of substrates were treated with 1 under thermal conditions. In most of the cases, dehydrogenation occurred. The results obtained are given in the Table-1.



1



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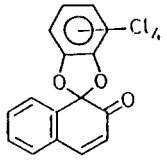
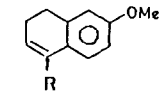


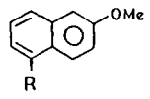
3

The spironaphthalenones 2 and 3 under thermal as well as photolytic[10] conditions isomerise to one another. The isomerisation is in fact an equilibrium process , with the equilibrium being in favour of 2. A free radical pathway has been considered for this isomerisation. The proposed radical intermediate should be able to abstract hydrogens as in the case of 1 and make available yet another method of dehydrogenation . A variety of dihydro compounds were reacted with the naphthalenone 2 under the thermal conditions (refluxing mesitylene temperature). The results obtained are summarised in the Table-1. The dehydrogenation could be effected either with 2 or 3, or a mixture of the two ; however, there was not much difference in the yields of the aromatised compounds .

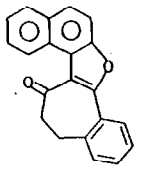
Utilising the enones (a mixture of 2 & 3 mostly), a formal synthesis of equilenane derivative 11 has been achieved. It was interesting to note that when molar quantities of 10 and the mixture of enones was used, in addition to the expected product 11, one more further dehydrogenated product 9 was obtained (in 2:1 ratio). However, when a mixture of 2 & 3, and 10 in the ratio of 2:1 was used, compound 9 was exclusively obtained. We could also obtain 9 by dehydrogenation of 8. When dehydrogenation of dihydropapaverine 14, with a mixture of 2 and 3 was carried out, papaveraldine 15 was obtained as the only product. This might have been obtained by further oxidation of the initially formed papaverine 16. The aromatisation of 1-Phenyl-3,4-dihydronaphthalene has been reported using S at a temperature of 270-280°C.[11] We have been able to achieve the same at a considerably lower temperature.



4a R = H
b R = CH_3
c R = i-Pr
d R = OAc



5a R = H
b R = CH_3
c R = i-Pr
d R = OAc



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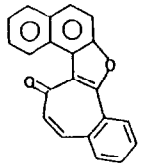

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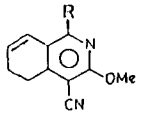
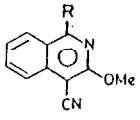
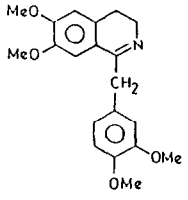


6a R = Me
b R = OMe



7a R = Me
b R = OMe



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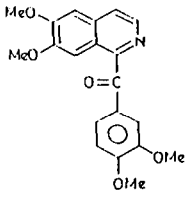

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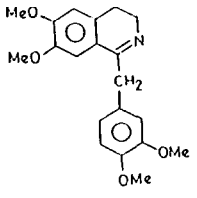

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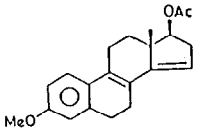

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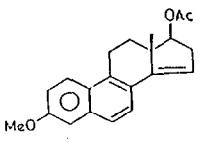

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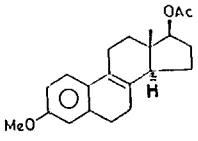

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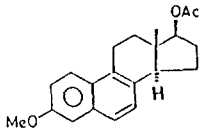

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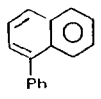

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As seen from the Table-1, the overall yields are better with naphthalenones 2 & 3 . This could be rationalised on the basis that the initially formed radical from 1 could participate in other competing reactions.[9b]

Tetralin, on treatment with even a large excess of this reagent, a mixture of 2 & 3, did not under go dehydrogenation. As a consequence of dehydrogenation of only the dihydroaromatic rings by spironaphthalenones 2 & 3, they could be used to effect regioselective dehydrogenation.

Table-1

substrate	product	yields [2 +3] yield	time(hrs)	[1] yield	time(min)
4a	5a	80 %	1/2	40 %	10-15
4b	5b	75-80 %	1/2	45 %	10-15
4c	5c	65 %	1/2	-	-
4d	5d	65 %	1/2	33 %	15
6a[12]	7a	65-70 %	1	40 %	20
6b[12]	7b	65-70 %	1	40 %	20
8[14]	9	65 %	2		
10[14]	11	65(9 + 11)%	2		
12[13]	13	50 %	1		
14[18]	15	60 %	2		
17[11]	18	65 %	2		

EXPERIMENTAL

All melting points are uncorrected. IR (Cm^{-1}) spectra were recorded on a HITACHI model 270-50 Infrared spectrometer. NMR spectra were recorded on a Jeol FX-90 Q spectrometer with Me_4Si as internal standard (δ = 0 ppm). MS (70 eV) were recorded on a Jeol MS-DX 303 spectrometer fitted with a built-in direct inlet system.

General Procedure: A mixture of 1 mole of the dihydroaromatic substrate and 1.1 mole of the spirocompound was refluxed in mesitylene for 1-2 hrs or till the reagent disappeared . The solvent was removed *in vacuo* and the residue dissolved in benzene. The product was purified by column chromatography over neutral alumina . The less polar fraction (benzene) gave the required aromatised product. The products were identified by comparison with the authentic spectra.

Reaction of 8 with naphthalenones 2 & 3

A mixture of 8 (200 mg,0.62 mmole) and the naphthalenones, 2 & 3, (270 mg,0.67 mmole) was refluxed in mesitylene for 2 hrs till the starting naphthalenones disappeared completely. It was cooled ,the solvent removed *in vacuo*. The residue was dissolved in benzene and chromatographed over neutral alumina. The benzene fraction gave a product identified as 9[16] [I.R (nujol) 1740 and 1623; ^{1}H NMR (90 MHz,$CDCl_3$) 1.05 (s,3H), 1.8 (m,1H), 2.16 (s,3H), 2.3-3.3 (m,5H),3.96 (s,3H), 5.16 (t, J = 9Hz,1H), 5.97 (t, J = 3.6Hz,1H),7.2 (m,3H), 7.6 (s,1H), 7.9 (d, J = 10Hz,1H); MS: m/e 322 (M^+,4), 262 (M-60,100)] (135 mg).

Reaction of 10 with 2 & 3

A mixture of 10 (200 mg,0.6 mmole) and a mixture of 2 & 3 (270 mg) was refluxed in mesitylene for about 2 hrs . After the usual work up , the benzene fraction was found to contain two compounds (nmr) which were purified by fractional crystallisation. The solid that crystallised out first was found to be the expected product 11. [I.R (nujol) 1737 and 1621; ^{1}H NMR (90 MHz,$CDCl_3$) 0.8 (s,3H), 1.8 (m,4H), 2.1 (s,3H), 2.3-3.2 (m,5H), 3.95 (s,3H), 4.9 (t,J = 9Hz,1H), 7.2 (m,3H), 7.6 (s,1H),7.8(d,J=10.1Hz,1H); MS: m/e 324 (M^+,90), 262 (M-62,100). It was further identified by its reduction to alcohol. m.p 175-6^{o}C (lit.[15] m.p. 179-180^{o}C). The other product was found to be 9.

Reaction of 14 with 2 & 3

A mixture of 14 (200 mg,0.59 mmole) and 2 & 3 (250 mg) was refluxed in mesitylene for 2 hrs . After the usual work up, the residue was chromatographed over neutral alumina. Elution with 5% EtOAc-$CHCl_3$ gave papaveraldine [m.p.208^{o}C (115 mg)], identified by spectral comparison.[17]

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