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N,N-DIETHYLHYDROXYLAMINE. A VERSATILE REAGENT FOR REDUCING QUINONES TO QUINOLS

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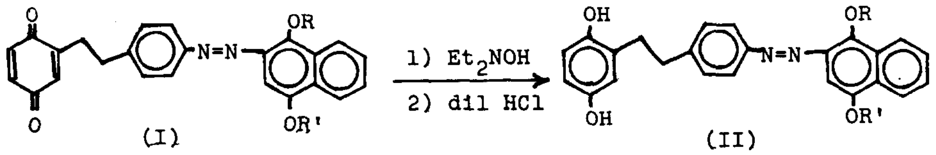
Reduction of quinones into quinols has ever been effected with various reducing agents, e.g., $SnCl_2$, Zn-AcOH, Fe-HCl, $Na_2S_2O_4$, $NaBH_4$, and molecular hydrogen.$^{1)}$ However, their reactions are often difficult to control, when starting quinones contain another reducible group or an easily hydrolyzable group. In the present communication, N,N-diethylhydroxylamine (DEH)$^{2)}$ will be reported to be a versatile reagent for reducing quinones.

Table 1 summarizes the results of DEH reduction of 1,4-benzoquinones and 1,4-naphthoquinone. The reduction proceeds smoothly under neutral conditions and affords good yields of mono- to tetrasubstituted hydroquinones. It is to be noted that the selective reduction of quinonyl group can be attained and that azo and acetoxy groups contained in substrates (Ia-If)$^{3,4)}$ remain unchanged through the reduction. DEH itself is considered to be converted into the corresponding nitrone, $MeCH{=}N^+(-O^-)Et$, which appears to form a 1:1 complex salt with the resulting quinol and to decompose on following treatment with a diluted acid. In fact, the 1:1 complex between 2-(p-tolyl)hydroquinone and the nitrone was precipitated as white crystals (mp 97-98°C, Anal. Found: C, 71.23; H, 7.28; N, 4.84% ($C_{17}H_{21}NO_3$)), when DEH reduction of 2-(p-tolyl)-1,4-benzoquinone was performed in benzene.$^{5)}$



(I) (II)

a: R = H, R' = i-Pr, b: R = H, R' = $MeOCH_2CH_2$, c: R = H, R' = $EtOCH_2CH_2$,
d: R = Ac, R' = i-Pr, e: R = Ac, R' = $MeOCH_2CH_2$, f: R = Ac, R' = $EtOCH_2CH_2$

Table 1. Reduction of Quinones with N,N-Diethylhydroxylamine

Substrate	Reaction Condition	Yield(%)	Product	mp(°C)
1,4-Benzoquinone	a)	66	Hydroquinone[b]	170-171
2-Phenyl-1,4-benzoquinone	a)	81	2-Phenylhydroquinone[b]	97-98
2-(p-Tolyl)-1,4-benzoquinone	a)	83	2-(p-Tolyl)-hydroquinone[b]	120-121
Duroquinone	c)	81	Durohydroquinone[b]	240-243 (sintered 235°C)
Bromotrimethyl-1,4-benzoquinone	c)	82	Bromotrimethylhydroquinone[b]	170-172 (dec)
Chloranil	a)	95	Tetrachlorohydroquinone[b]	243-245 (sintered 236°C)
Ia[d]	a)	80	IIa[d]	222-224
Ib[d]	a)	66	IIb[d]	176-178
Ic[d]	a)	85	IIc[d]	142-144
Id[d]	a)	70	IId[d]	161-161.5 (dec)
Ie[d]	a)	83	IIe[d]	168-169
If[d]	a)	82	IIf[d]	172-173 (dec)
1,4-Naphthoquinone	a)	83	1,4-Naphthohydroquinone[b]	165-167

a) Stirred in AcOEt at room temp. b) Identified with an authentic sample. c) Refluxed in AcOEt. d) All the new compounds gave correct analyses.

The following procedure for the preparation of 2-(p-tolyl)hydroquinone is representative and may reveal the convenience and usefulness of DEH reduction. DEH (2.50 g, 28 mmoles) was added at room temperature to a stirred suspension of 2-(p-tolyl)-1,4-benzoquinone (4.95 g, 25 mmoles) in AcOEt (50 ml). The resulting solution was stirred for 40 min, washed successively with ca 4% HCl and with water, and dried over Na_2SO_4. Concentration and recrystallization from benzene–n-hexane (1:8) gave 2-(p-tolyl)hydroquinone (4.10 g, 83%).

References and Footnotes

1) V. Migrdichian, "Organic Synthesis," Vol. 2, pp. 1312-1313, Reinhold Publishing Co., New York (1957). 2) For the preparation, see W. Ruppert, Ger. 1 004 191 (1957); Chem. Abstr., 54, 584c (1960). 3) For the preparation, see S. Fujita, Ger. Offen., 2 413 223 (1974). See also S. Fujita, K. Sano, and N. Furutachi, Ger. Offen., 2 413 189 (1974). 4) Azo dyes having a hydroquinone moiety such as IIa-IIf are referrred to as dye developers, which are important components in color diffusion transfer reversal photography. 5) Similar complexes have been reported in M. A. T. Rogers, Nature, 177, 128 (1956).

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