The Stability of Aryl-t-butylnitroxides

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WE have shown previously[1] that phenyl-t-butylnitroxide (I; Ar = Ph) spontaneously disproportionates during isolation to the corresponding secondary amine and quinone-imine *N*-oxide (II). The present report deals with the relative stabilities and mechanism of decomposition of a number of alkyl-substituted phenyl-t-butylnitroxides prepared by treatment of t-nitrosobutane with the appropriate aryl Grignard reagent and oxidation of the hydroxylamine so formed.

Stable, isolable aryl-t-butylnitroxides were obtained when: (i) the *para*-position was blocked by a t-butyl or phenyl group; (ii) the *para*-position was sterically hindered by two *meta*-methyl substituents (with one *meta*-methyl group the rate of disproportionation merely decreased); (iii) the aryl group was twisted out of conjugation with the nitrogen atom to some extent by one or two *ortho*-methyl substituents, unpaired electron density at the *para*-position being reduced as a result.†

p-Ethyl- and *p*-isopropyl-phenyl-t-butylnitroxides (I; Ar = *p*-EtC_6H_4 and *p*-$Pr^iC_6H_4$) were not sufficiently stable to be isolated. In concentrated solution they disproportionated rapidly to the corresponding hydroxylamines and methide *N*-oxides (III; $R^1 = H$, $R^2 = Me$ and $R^1 = R^2 = Me$)

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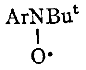
† Stable alkylarylnitroxides are also obtained when the t-alkyl group is large as in phenyl-*trans*-decalylnitroxide (ref. 2) and the Banfield and Kenyon radical (ref. 3).

TABLE

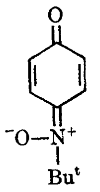
Hyperfine coupling constants (*in gauss* ± 0·1) *of aryl-t-butylnitroxides* (I)

Ar	a_N	$a_{o\text{-H}}$	$a_{p\text{-H}}$	$a_{m\text{-H}}$	$a_{\text{substituent}}$
Ph	12·30	2·05	2·05	1·00	—
p-Me·C_6H_4	12·75	1·90	—	0·95	a_H = 1·90
p-Et·C_6H_4	12·45	1·95*	—	1·00*	a_H = 1·60*
p-Pr^i·C_6H_4	12·50	1·90	—	0·95	a_H = 0·95
p-$PhCH_2$·C_6H_4	12·30	2·10	—	1·00	a_H = 1·60
p-Ph_2CH·C_6H_4	12·15	2·10	—	1·05	a_H = 1·65
p-Me_3C·C_6H_4	12·40	2·20	—	1·00	—
p-Ph·C_6H_4	11·90	2·50	—	1·10	—
m-MeC_6H_4	12·60	1·95	1·95	0·65	a_H = 0·65
3,5-Me_2·C_6H_3	12·70	1·80	1·80	—	a_H = 0·60
o-Me·C_6H_4	13·50	each component of the triplet had about 22 narrowly spaced lines			
2,6-$Me_2C_6H_3$	13·40	each component of the triplet had about 28 narrowly spaced lines			
p-OHC·C_6H_4	10·80	2·35	—	0·95	—
Dimer (IV; R^1=H,R^2=Me)	12·25	1·95	—	1·00	a_H = 1·00
Dimer (IV; R^1=R^2=Me)	12·20	1·90	—	0·95	—
Dimer (IV; R^1=H,R^2=Ph)	12·10	2·00	—	1·00	a_H = 1·00
Trimer (V; R=H,R^2=Ph)	12·15	1·95	—	0·95	a_H = 1·00

* Provisional values.



(I)



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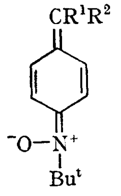

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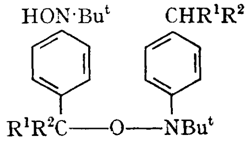

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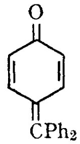

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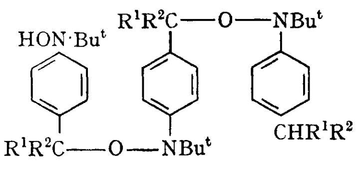

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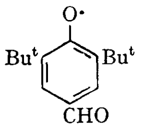
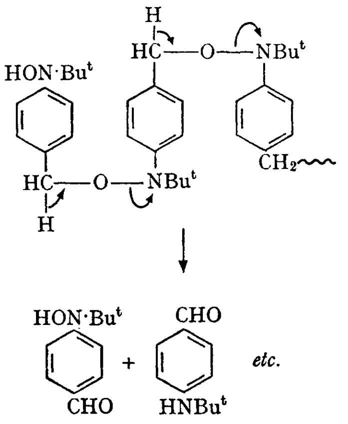


(X)

which combined readily to give the dimers (IV; R^1=H, R^2=Me and R^1=R^2=Me). p-Benzylphenyl-t-butylnitroxide (I; Ar=p-$PhCH_2$·C_6H_4) decomposed to a mixture of dimer (IV; R^1=H, R^2=Ph) and trimer (V; R^1=H,R^2=Ph). In this case the intermediate methide (III; R^1=H,R^2=Ph) is longer-lived and adds both monomeric and dimeric hydroxyl amines. The methide from p-diphenylmethylphenyl-t-butylnitroxide (I; Ar=Ph_2CH·C_6H_4) was even more stable and could be isolated from the decomposition mixture; in the presence of light it decomposed to fuchsone[4] (VI). The structures assigned to the dimers and trimer were based on analytical, molecular weight (osmometric), i.r., n.m.r., (Ar·CH·O· absorption in the region τ 6·0) and chemical evidence (all gave a positive hydroxylamine–tetrazolium test[5]). In



(VII)

(VIII) (IX)

addition, the e.s.r. spectra of the nitroxides formed from these hydroxylamines showed coupling with one proton less than those of the parent nitroxides (see Table).

The decomposition of t-butyl-*p*-tolylnitroxide (I; Ar=*p*-Me·C_6H_4) was more complicated and gave a complex mixture of products from which the parent hydroxylamine, and the aldehydes (VIII) and (IX) (as the 2,4-dinitrophenylhydrazone) were isolated. These products probably arise by degradation of polymeric hydroxylamines (VII) formed by self-condensation of the highly reactive methide (III; $R^1=R^2=H$) (*cf.*, the polymerization of *p*-benzoquinonemethide[6]).

Details of the e.s.r. spectra of the nitroxides, measured in carbon tetrachloride solution, are given in the Table. The a_N values of *ortho*-substituted radicals were predictably higher than those of the others but no major splitting due to the protons of the *ortho*-methyl group was detected. Thus the quartet splitting observed in the spectrum of phenyl-*o*-tolylnitroxide and attributed[7] to a "through space" coupling with the *ortho*-methyl protons almost certainly results from equal interaction of the unpaired electron with the *ortho*- and *para*-protons of the unsubstituted ring. The spectrum obtained from the aldehydic nitroxide (I; Ar=*p*-OCH·C_6H_4) differed considerably from that previously attributed[8] to this radical, showing only a very small coupling with the aldehydic proton [*cf.*, the spectrum of the phenoxyl (X)].[9]

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