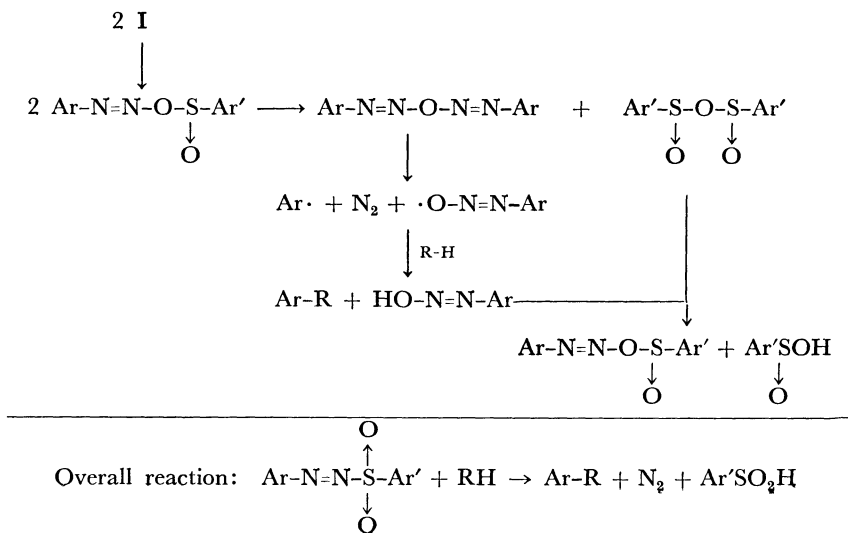




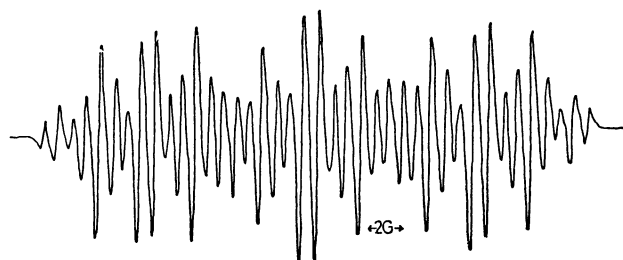


Fig. 1(a). The ESR spectrum of an irradiated mixture of *p*-MeOC₆H₄N=NO₂SC₆H₄Me-*p* and PhCH=N-Ph in benzene.

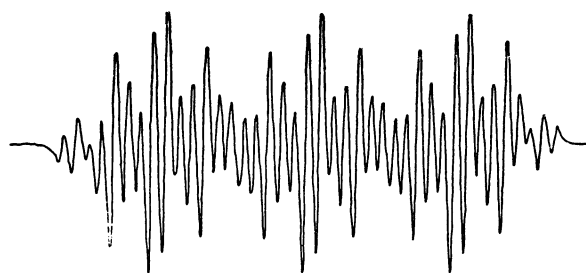
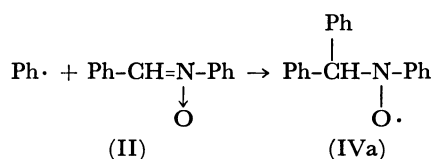
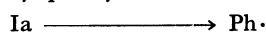


Fig. 1(b). An ESR spectrum obtained by simulation using $A_N = 10.01$, $A_{\beta-H} = 3.41$, $A_{o-H} = 2.51$, $A_{m-H} = 0.88$, and $A_{p-H} = 2.51$ G.

culated from analysis of the hyperfine splittings.

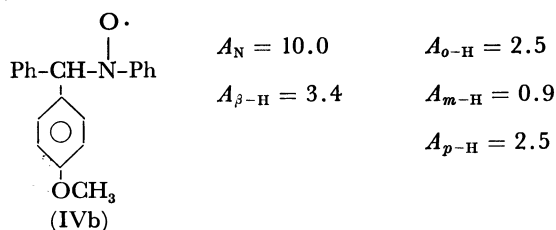
$$\begin{array}{ll} A_N = 10.01 & A_{o-H} = 2.51 \\ A_{\beta-H} = 3.41 & A_{m-H} = 0.88 \\ & A_{p-H} = 2.51 \\ & g = 2.0056 \end{array}$$

Simulation was carried out by using these hyperfine splitting constants, the result (Fig. 1b) being in excellent agreement with what was experimentally observed. Thus the radical responsible for the ESR pattern is benzhydryl phenyl nitroxide radical (IVa) shown below.



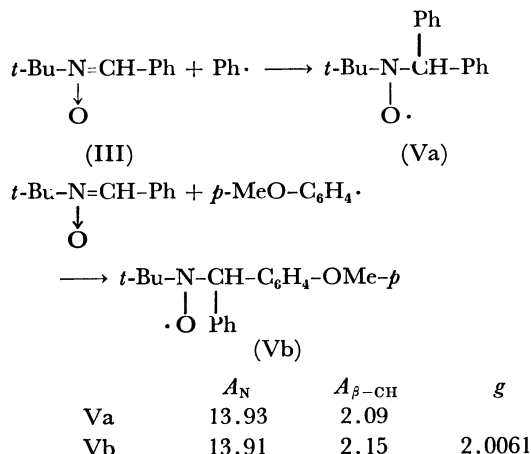
Bluhm and Weinstein¹⁰) trapped the phenyl radical, produced from phenylazotriphenylmethane, by the reaction with II, and the hyperfine splitting constants they reported for radical IVa are approximately the same as those described above.

When Ib was decomposed by irradiation or by heating in the presence of II, ESR signals ascribable to nitroxide radical IVb were observed. The following hyperfine splitting constants were obtained from the analysis of the ESR pattern.



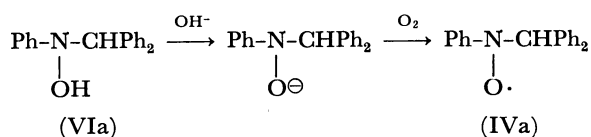
When the samples were irradiated at room temperature and the ESR signals were examined after the light was turned off, they were observable for about 15 min. This indicates that radicals IVa and IVb are fairly stable.

ESR studies on the reaction between Ia and nitron III and that between Ib and III showed the presence of nitroxide radicals Va and Vb, respectively. The following hyperfine splitting constants were obtained.

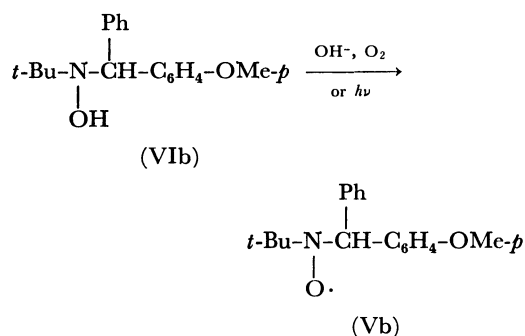


Concerning Va, Janzen and Blackburn reported that $A_N = 13.73$ and $A_{\beta-H} = 2.08$ G.¹¹)

In order to prove the structure of IVa, *N*-benzhydryl-*N*-phenylhydroxylamine (VIa) was synthesized from nitron II and phenylmagnesium bromide, and was oxidized with air in a weakly alkaline (NaOH) aqueous ethanol. The ESR signals observed were exactly the same as those observed when Ia was photolyzed in the presence of II. When VIa was treated with *n*-BuLi in benzene and then irradiated with a high pressure mercury lamp in the presence of air, similar ESR signals ascribable to nitroxide radical IVa were observed.

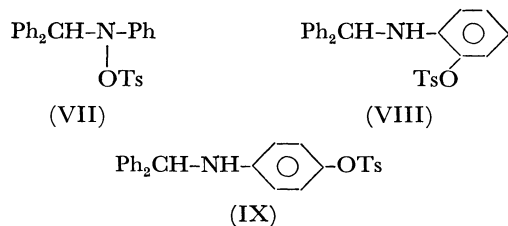


In a similar manner, when an alkaline ethanol solution of *N*-*t*-butyl-*N*-(phenyl-*p*-methoxyphenylmethyl)hydroxylamine (VIb) was oxidized with air or irradiated in the presence of air, nitroxide radical Vb was formed and its ESR signals were identical with those obtained from azosulfone Ib and nitron III.

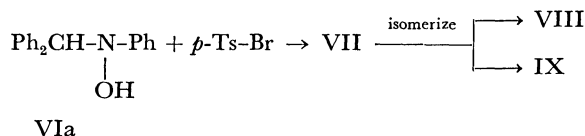


These data obtained by means of ESR have established that aryl free radicals are formed by thermolysis or photolysis of azosulfones Ia or Ib.

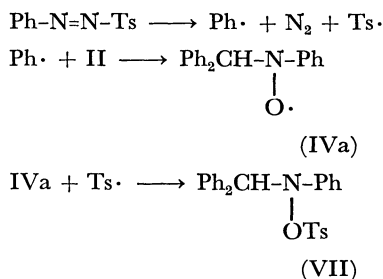
In order to determine the final products from nitroxide radicals IV and V, a mixture of Ia, pyridine (3 mol/mol Ia; added in order to keep the medium weakly alkaline) and nitron II (1.5 mol/mol Ia) was thermolyzed. Recrystallization of the products gave a compound, which appeared to be *N*-benzhydryl-*N*-phenylhydroxylamine *O*-*p*-toluenesulfonate (VII). It was very unstable, readily isomerizing to *o*- and *p*-benzhydrylaminophenyl *p*-toluenesulfonates (VIII) and (IX), when allowed to stand at room temperature. When the products of thermolysis of Ia-II-pyridine in benzene were separated by column chromatography, VII was not detected and VIII and IX were isolated in 17% and 1% yields (per 100 mol Ia), respectively.



When *N*-benzhydryl-*N*-phenylhydroxylamine (VIa) was allowed to react with *p*-tosyl bromide in pyridine at room temperature, VII was not obtained; isomerization took place during the course of recrystallization and the product isolated was VIII. A similar rearrangement of hydroxylamine-*O*-esters has been reported.¹²⁾



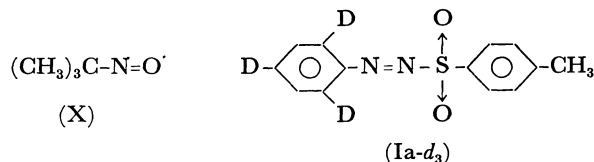
The formation of VII can be ascribed to a combination of nitroxide radical IVa and *p*-toluenesulfonyl radical.



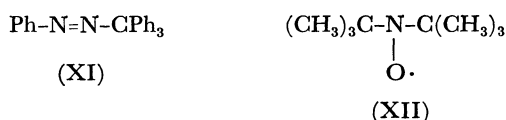
The fact that VII is formed proves indirectly that the decomposition of azosulfone Ia yields *p*-toluenesulfonyl radical in addition to phenyl radical.

In an attempt to trap *p*-tosyl radical with nitron III, Ia was photolyzed in the presence of excess III at room temperature under various conditions. The presence of two new nitroxide radicals in addition to Va were detected by ESR; $A_N=12.5$ G and 7.67 G (for Va, $A_N=13.93$ G). Since these two radicals showed simple triplets without hyperfine splittings due to β -hydrogens, addition of radicals on some nitroso compounds containing only *t*-butyl groups was suspected. When an ethereal solution of Ia was irradiated at 366 nm in the presence of 2-methyl-2-nitrosopropane(X), ESR signals of two radicals were observed; $A_N=12.5$ G and

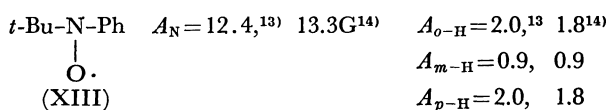
15.5 G, and $g=2.0060$ for both. In order to determine whether or not these radicals arose from trapping of phenyl radical, *p*-tolyl 2,4,6-trideuteriophenylazo sulfone (Ia- d_3) was photolyzed in the presence of X. Since the radicals detected were identical with those formed in the case of Ia, they cannot be the products of trapping of phenyl radical with X.



When phenylazotriphenylmethane (XI), another phenyl radical source, was photolyzed in ether in the presence of X, two radicals were detected; one with $A_N=12.8$ G and $A_{\beta-\text{CH}}=2.6$ G and the other with $A_N=15.5$ G. When X was irradiated in ether with a sodium lamp (589 nm), the ESR signals obtained were a simple triplet with $A_N=15.5$ G. Therefore, the radical with $A=15.5$ G must be di-*t*-butyl nitroxide radical (XII).

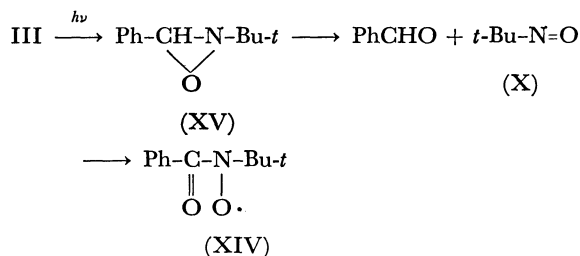


It has been reported that XII is formed by the photolysis of X; $A_N=15.7$ G¹³⁾ or 15.5 G,¹⁴⁾ and also that *t*-butyl phenyl nitroxide (XIII) formed by the trapping of phenyl radical with X shows hyperfine splittings due to *ortho* and *para* hydrogens of the benzene ring.^{13,14)}

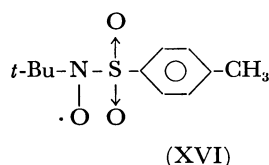


The fact that no XIII was found in the photolysis of Ia in the presence of X can be ascribed to the consumption of phenyl radical by abstraction of α -hydrogens of ether.

The radical with $A_N=7.67$ G formed in the photolysis of Ia in the presence of III is probably benzoyl *t*-butyl nitroxide radical¹¹⁾ (XIV) produced by the photolysis of III. It has been reported¹⁵⁾ that upon irradiation nitron III isomerizes to α -phenyl-*N*-*t*-butyloxazirane (XV), which then yields 2-methyl-2-nitrosopropane (X) and XIV.



Thus, of the three radicals produced from the photolysis of Ia in the presence of III, the one with $A_N=13.93$ G is Va, that with $A_N=7.67$ G is XIV, and that with $A_N=12.5$ G remains to be explained. If this is not XIII, the only possibility seems to be nitroxide radical XVI, which can be formed by the trapping of *p*-toluenesulfonyl radical with X. In order to confirm the



possibility, *p*-toluenesulfonyl iodide, another *p*-tosyl radical source, was irradiated at 589 nm in the presence of X. A nitroxide radical with $A_N=12.5$ G was observed, which is identical with that obtained in the photolysis of Ia or Ib in the presence of X.

The rate of decrease of the ESR signals of XVI was determined after light was turned off, and the nitroxide radical XVI was found to be a fairly stable radical with a half-life of 44 seconds. When an ethereal solution of X was irradiated in the absence of *p*-tosyl iodide, ESR signals observed were those of di-*t*-butyl nitroxide (XII) alone. The following reaction sequence is therefore plausible.

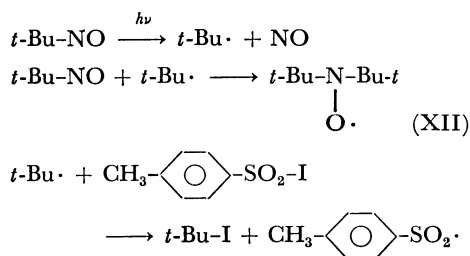


Fig. 2(a). The ESR spectrum of an irradiated mixture of $\text{PhN}=\text{NO}_2\text{SC}_6\text{H}_4\text{-Me-}p$ and $t\text{-Bu-N}=\text{CH-Ph}$

in benzene ($A_N = 13.13$, $A_{\beta-H} = 2.09$; $A_N = 12.5$; $A_N = 7.67$ G).

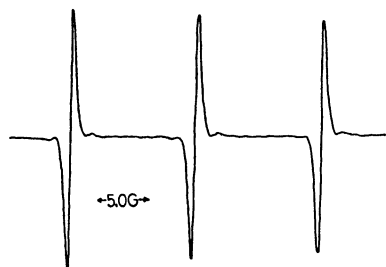
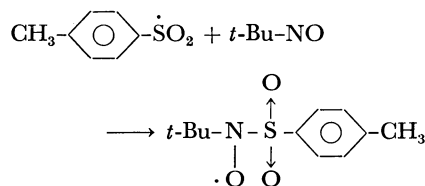
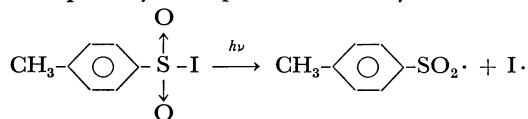


Fig. 2(b). The ESR spectrum of an irradiated solution of *t*-Bu-N=O in ether ($A_N=15.5G$).



It is possible that *p*-toluenesulfonyl radical is produced by direct photolysis of *p*-toluenesulfonyl iodide itself.⁶⁾



However, since X absorbs at longer wavelength region (near 589 nm), it seems more probable that the *t*-butyl radical produced by photolysis of X abstracts the iodine atom from *p*-tosyl iodide, yielding *p*-tosyl radical and *t*-butyl iodide.

When an ethereal solution of iodobenzene was irradiated in the presence of X, two sets of ESR signals were observed; a triplet with $A_N=15.5$ G and a triplet with $A_N=12.5$ G and with hyperfine splittings. The former is due to XII, and the latter can be ascribed to *t*-butyl phenyl nitroxide (XIII). The formation of XIII can be explained in terms of the following reaction steps: 1) photolysis of X gives *t*-butyl radical, 2) *t*-butyl radical abstracts the iodine atom from iodobenzene, and 3) the phenyl radical formed is trapped

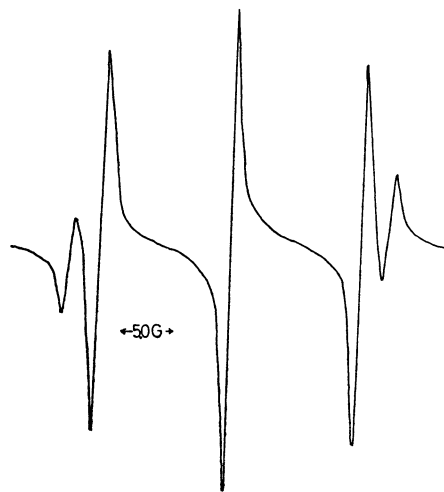


Fig. 2(c). The ESR spectrum of an irradiated mixture of $\text{PhN}=\text{NO}_2\text{SC}_6\text{H}_4\text{Me-}p$ and $t\text{-Bu-N=O}$ in ether ($A_N=12.5$, and $A_N=15.5\text{G}$).

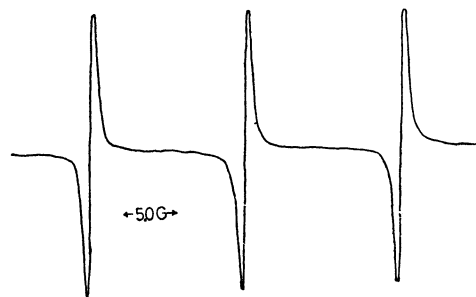


Fig. 2(d). The spectrum of an irradiated mixture of *p*-MeC₆H₄SO₂I and *t*-Bu-N=O in ether ($A_N=12.5$ G).

by X. In contrast with the case of the photolysis of azosulfone Ia in the presence of X, phenyl radical was trapped by X in the photolysis of iodobenzene. In this case, iodobenzene was used in a high concentration, and therefore not all of the phenyl radicals produced were consumed by the reaction with ether.

Thus, the spin trapping experiments with nitrones II, III and 2-methyl-2-nitrosopropane (X) have proved that aryl radicals and sulfonyl radicals are produced by the thermolysis or photolysis of azosulfones Ia or Ib.

Experimental

Materials. Arylazo *p*-tolyl sulfones were synthesized by the addition of aqueous solutions of *p*-toluenesulfinate to aqueous solutions of arenediazonium salts,⁴⁾ and recrystallized from methanol. Nitrone II was produced by the condensation of phenylhydroxylamine with benzaldehyde, and recrystallized from ethanol. Nitrone III was synthesized by the following two steps; 1) H₂O₂(90%)-Ac₂O-oxidation of benzylidene-*t*-butylamine to 2-*t*-butyl-3-phenyloxaziridine and 2) isomerization of the oxaziridine by refluxing in acetonitrile for 2 days.¹⁶⁾ It was recrystallized from hexane; mp 76 °C.

ESR Measurements. ESR signals were observed by use of a JES-ME-1X.

Formation of Benzhydryl Phenyl Nitroxide Radical IVa.

Benzhydryl bromide, phenylhydroxylamine and sodium acetate were ground in a porcelain mortar. When the mixture was washed with water and then with hexane and the residue was recrystallized from benzene-hexane, *N*-benzhydryl-*N*-phenylhydroxylamine (VIa) was obtained. This hydroxylamine was also synthesized from α ,*N*-diphenyl nitrone II and phenylmagnesium bromide.

Oxidation of VIa with HgO or 2,6-dichlorophenol-indophenol sodium was attempted, but was not successful. However, when air was bubbled through a weakly alkaline (NaOH) aqueous ethanol solution of VIa, ESR signals were observed. The same ESR signals were observed when a benzene solution of VIa containing some *n*-butyl lithium was irradiated with a high pressure mercury lamp. The hyperfine splittings of the ESR signals were identical with those obtained from azosulfone Ia and nitrone II, and are ascribable to benzhydryl phenyl nitroxide radical IVa.

Formation of *t*-Butyl Phenyl-*p*-methoxyphenylmethyl Nitroxide Radical IVb.

N-*t*-Butyl-*N*-(phenyl-*p*-methoxyphenylmethyl) hydroxylamine (VIb) was prepared from α -phenyl *N*-*t*-butyl nitrone and *p*-methoxyphenylmagnesium bromide, and was oxidized by air in a weakly alkaline (NaOH) aqueous ethanol solution. The ESR signals observed were identical with those obtained in the reaction between azosulfone Ib and nitrone III, and are ascribable to *t*-butyl phenyl-*p*-methoxyphenylmethyl nitroxide radical IVb.

Products of the Reaction between Azosulfone Ia and Nitrone II.

A mixture of Ia (2.5 g), II(4.0 g), pyridine (4.0 g) and benzene (130 ml) was heated at 91 °C for 3 hr (the half-life of Ia under these conditions is 46 min). The reaction mixture was washed with water and with dilute HCl for removal of pyridine, and then concentrated. The column chromatography (Florisil) of the residue gave biphenyl 10.8, azo-

benzene 6.1, *o*-benzhydrylaminophenyl *p*-toluenesulfonate (VIII) 17.2 and *p*-benzhydrylaminophenyl *p*-toluenesulfonate (IX) 1.0 mol/100 mol Ia.

Synthesis of VIII. *o*-Nitrophenyl *p*-toluenesulfonate was reduced with SnCl₂-HCl, and the *o*-aminophenyl *p*-toluenesulfonate obtained (1.5 g) was heated with benzhydryl chloride (1.0 g) and pyridine (5 ml) at 90 °C for 3 days. The reaction mixture was washed with water and then with dilute HCl, and pyridine was distilled off under reduced pressure. Recrystallization of the residue from hexane-benzene gave VIII; mp 122–123 °C.

Synthesis of IX. A mixture of *p*-aminophenyl *p*-toluenesulfonate (1.5 g), benzhydryl chloride (1.0 g) and pyridine (5 ml) was refluxed for 13 hr and then treated in a manner similar to that described for VIII. Recrystallization from hexane-benzene gave IX; mp 133–134 °C.

Analysis:	C	H	N	M.W.
VIII (authentic)	72.38	5.37	3.13%	
VIII (from Ia and II)	72.87	5.43	3.09	419
IX (authentic)	71.21	5.31	2.99	
IX (from Ia and II)	69.85	5.31	3.41	421
Calcd.	72.8	5.4	3.3	429

Molecular weights were determined by use of the vapor pressure method with a Hitachi-Perkin Elmer Molecular Weight Apparatus 115.

Footnotes

- 1) Organic Sulfur Compounds. Part 50.
- 2) C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, **82**, 108, 117 (1960).
- 3) M. Kobayashi, S. Fujii, and H. Minato, *This Bulletin*, **45**, 2039 (1972).
- 4) M. Kojima, H. Minato, and M. Kobayashi, *ibid.*, **45**, 2032 (1972).
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- 6) J. M. Squire and W. A. Waters, *J. Chem. Soc.*, **1962**, 2068; C. M. M. de Silva Correa, A. S. Lindsay, and W. A. Waters, *J. Chem. Soc., C*, **1968**, 1874.
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- 8) C. Rüchardt and E. Merz, *Tetrahedron Lett.*, **1964**, 2431; C. Rüchardt and B. Freudenberg, *ibid.*, **1964**, 3623.
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- 12) R. Huisgen and F. Bayerlein, *Ann. Chem.*, **630**, 138 (1960).
- 13) A. Mackor, Th. A. J. W. Majer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Lett.*, **1966**, 2115.
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- 15) A. L. Bluhm and J. Weinstein, *J. Amer. Chem. Soc.*, **92**, 1444 (1970).
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