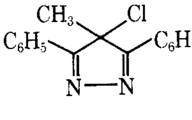
Table I. Elemental Analyses[a]

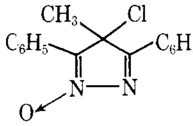
	Calcd, %				Found, %			
Compd	C	H	N	Cl	C	H	N	Cl
1	71.51	4.88	10.42	13.19	71.38	4.91	10.60	13.11
2	67.49	4.60	9.84		67.52	4.72	10.10	
3	63.90	4.36	9.31	11.79	65.70	4.47	9.36	11.98
4	77.25	6.10	10.60		77.25	6.22	10.68	
5	72.84	5.75	9.99		72.73	5.94	9.97	
6	68.91	5.44	9.45		68.62	5.38	9.60	
8	64.87	4.80	8.90	11.26	64.66	4.86	8.89	11.54
9	63.90	4.36	9.31	11.79	63.70	4.47	9.36	11.98

[a] Compounds **10** and **11** were analyzed by mass spectrometer peak matching because only small amounts were available. Calcd for $C_{18}H_{18}N_2O_3$ (**10**): 310.1318. Found: 310.1283. Calcd for $C_{17}H_{10}N_2O_3$ (**11**): 296.1162. Found: 296.1122.

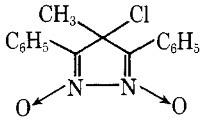
obtained by the action of *tert*-butyl hypochlorite or gaseous chlorine on the parent heterocycle.[4] All react with methanolic sodium hydroxide[5] to produce the corresponding 4-methoxymethylpyrazole derivatives, **4**, **5**, and **6**,[6] in yields of 80–95%. These transformations are accompanied by the disappearance of the CCH_3 (δ 2.00–2.18) groups from the NMR spectra, the appearance of OCH_3 (3.42) groups, and the appearance of the low field NH and OH resonances (13.1).



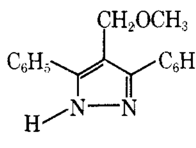
1, mp 115–117 °C



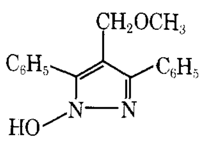
2, mp 109–111 °C



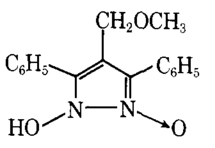
3, mp 140–142 °C



4, mp 181–183 °C

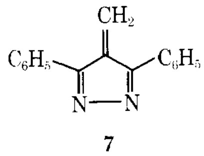


5, mp 157–158 °C



6, mp 183–184 °C

It seems likely that these reactions proceed by an elimination–addition mechanism with the diazafulvene **7** (and its *N*-oxide derivatives) as an intermediate. Burgess and Sanchez have reported the synthesis of the diphenylmethylene analogue of **7** and its reaction with methanol to yield the 4-methoxydiphenylmethylpyrazole.[7]



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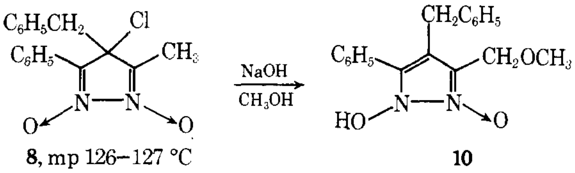
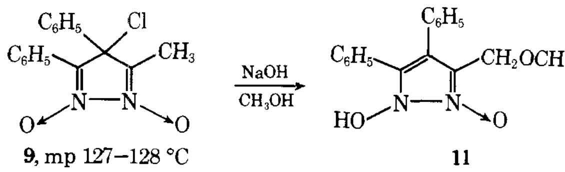
In a somewhat more unusual reaction, treatment of chlorides **8** and **9** in the same manner led to side-chain substitution in the 3-methyl group yielding compounds **10** and **11**. This result suggests that the enhanced acidity of these methyl groups leads to the formation of the 3-methylene derivative **12** in these cases.[8] The yields were much lower in these two examples and it is apparent that other destructive base-catalyzed reactions operate concurrently. Elemental analyses are given in Table I.



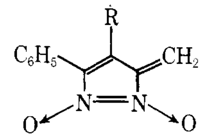
8, mp 126–127 °C

10



9, mp 127–128 °C

11



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(1) This research was supported in part by a grant from the National Cancer Institute, National Institutes of Health, Grant No. CA-10742.
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(5) Compound **3** gave the corresponding ethyl ether when ethanolic NaOH was used.
(6) Treatment of 3,4,5-trimethylpyrazole with bromine in methanol produces 3-methoxy-3,4,5-trimethyl-3*H*-pyrazole: G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966).
(7) E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, **39**, 940 (1974).
(8) Steric factors also must be involved in the case of compound **8**, since its 4-methyl analogue undergoes the normal reaction leading to the 4-methoxymethyl derivative.

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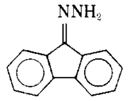
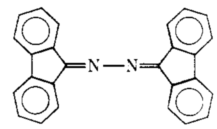
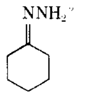
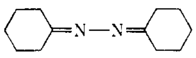
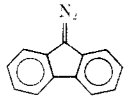
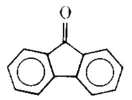
The Reaction of Superoxide with Hydrazines, Hydrazones, and Related Compounds[1]

Summary. Potassium superoxide reacts with various hydrazo compounds and certain related substances in a variety of ways: monosubstituted arylhydrazines are readily oxidized in a reaction which appears to involve free aryl radicals; 1,2-diarylhydrazines are converted to the corresponding azo compound; certain 1,1-disubstituted hydrazines are oxidized to *N*-nitroso amines; and certain hydrazones are converted into the corresponding azine.

Sir: The autoxidation of hydrazines and certain related substances is a well-known but little understood reaction.[2] The redox nature of such processes suggests the possibility that superoxide may be involved.[3,4] In an effort to define the potential role of superoxide in these reactions we have examined

Table I. Reaction of Hydrazines, Hydrazones and Related Compounds with Superoxide[a]

Entry	Substrate	Solvent	Reaction time, h	Product yields (%)[b,c]
1	$C_6H_5NHNH_2$	$C_6H_5CH_3$	16	C_6H_6 (81)
		C_6H_6	16	$(C_6H_5)_2$ (16)
		Me_2SO	16	C_6H_6 (85)
2	$p\text{-}CH_3C_6H_4NHNH_2$	C_6H_6	18	$C_6H_5CH_3$ (61) $p\text{-}CH_3C_6H_4C_6H_5$ (22)^d
3	$p\text{-}ClC_6H_4NHNH_2$	C_6H_6	18	C_6H_5Cl (48) $p\text{-}ClC_6H_4C_6H_5$ (38)^c
4	$C_6H_5CH_2NHNH_2$	C_6H_6	24	$C_6H_5CH_3$ (54) $C_6H_5CO_2H$ (15)^d C_6H_5CHO (6) $C_6H_5CH_2OH$ (8)
5	$n\text{-}C_8H_{17}NHNH_2$^{e}	C_6H_6	24	$n\text{-}C_8H_{18}$ (32)
6	$C_6H_5NHNHC_6H_5$	C_6H_6	24	$C_6H_5N{=}NC_6H_5$ (98)
7	$(o\text{-}CH_3C_6H_4)NHNH(C_6H_4CH_3\text{-}o)$	C_6H_6	8	$(o\text{-}CH_3C_6H_4)N{=}N(C_6H_4CH_3\text{-}o)$ (85)^d
8	$(n\text{-}C_4H_9)NHNH(n\text{-}C_4H_9)$^{f}	C_6H_6	24	$(n\text{-}C_4H_9)N{=}N(n\text{-}C_4H_9)$ (<1)^g
			144	$(n\text{-}C_4H_9)N{=}N(n\text{-}C_4H_9)$ (<1)
9	$(C_6H_5)_2NNH_2$	C_6H_6	24	$(C_6H_5)_2NNO$^{h} (50)
10	$(C_6H_5)(CH_3)NNH_2$	C_6H_6	6	$(C_6H_5)(CH_3)NNO$^{i} (33) $(C_6H_5)(CH_3)NH$ (59)
11	$C_6H_5NHNHC(O)NH_2$	C_6H_6	2	$C_6H_5N{=}NC(O)NH_2$^{j} (80)^d
12	$C_6H_5C({=}NNH_2)CH_3$	C_6H_6	24	$C_6H_5(CH_3)C{=}NN{=}C(CH_3)C_6H_5$^{k} (91)^d
13	$C_6H_5C({=}NNH_2)C_6H_5$^{l}	C_6H_6	19	$(C_6H_5)_2C{=}NN{=}C(C_6H_5)_2$^{m} (83)^d
14		C_6H_6	2	 (77)^d
15		C_6H_6	144	 (<1)^g
16		C_6H_6	4	 (86)^d
17	$C_6H_5C({=}N_2)C_6H_5$	C_6H_6	30	$C_6H_5C(O)C_6H_5$ (<1)^g

[a] Reaction carried out at 25 °C. Unless otherwise indicated, a substrate concentration of 0.25 M and a molar ratio of KO_2/substrate = 3 was employed. [b] Yields were determined by GLC unless otherwise stated. [c] Products were identified by comparison of their IR and mass spectra with those of authentic samples as well as GLC retention times and melting points, where applicable. [d] Values based on isolated yield. [e] O. Westphal, *Chem. Ber.*, **74**, 759 (1941). [f] H. Feuer, G. B. Silvermann, H. P. Angstadt, and A. R. Fauke, *J. Org. Chem.*, **27**, 2081 (1962). [g] A substantial fraction (>90%) of unreacted starting substrate was recovered. [h] Mp 65–66 °C (lit. mp 65–66 °C: M. M. Chen, A. F. D'Adamo, Jr., and R. I. Walter, *J. Org. Chem.*, **26**, 2721 (1961). [i] "Organic Syntheses", Collect. Vol. II., Wiley, New York, N.Y., 1955, p 460. [j] Mp 112–114 °C (lit. mp 113–115 °C): H. Beck, E. Baltin, and J. Froner, *Chem. Ber.*, **99**, 3337 (1966). [k] Mp 119–121 °C (lit. mp 121.5 °C): U.S. Patent 3 153 089 (Oct 13, 1964); from *Chem. Abstr.*, **62**, 490b (1965). [l] R. Baltzly, N. B. Mehta, P. B. Russel, R. E. Brooks, E. M. Grivsky, and A. M. Steinbert, *J. Org. Chem.*, **26**, 3669 (1961). [m] Mp 162.5–3.5 °C (lit. mp 162.8–3.8 °C): S. S. Hirsch, *ibid.*, **32**, 3433 (1967). [n] Mp 263–268 °C (lit. 262–267 °C): J. Weisburger and P. H. Grandham, *ibid.*, **21**, 1160 (1956). [o] A. Pross and S. Sternhall, *Aust. J. Chem.*, **23**, 989 (1970).

and report here the reactivity of various hydrazo compounds towards superoxide.

The experimental procedures employed are typified by the following description of the reaction of potassium superoxide with 1,2-diphenylhydrazine. 1,2-Diphenylhydrazine (0.921 g, 5.00 mmol) was added in one portion to a mixture of 18-crown-6 ether[5a] (0.528 g, 2.00 mmol) and powdered potassium superoxide[5b] (1.42 g, 20.0 mmol) in dry benzene (20 ml) at 25 °C contained in a 50-ml flask equipped with a Teflon-coated stirring bar. The subsequent reaction was initially accompanied by a moderate evolution of oxygen; the resulting mixture was stirred vigorously for 24 h and then cautiously poured into 20-ml of water. This mixture was extracted with two 20-ml portions of benzene. The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The crude azobenzene, which was obtained in virtually quantitative yield, was recrystallized from 30% aqueous ethanol. Results obtained on similar treatment of other representative substrates are given in Table I.

These observations reveal that a variety of hydrazo compounds are readily oxidized by superoxide. Taken together, they suggest a picture of the reactivity of hydrazo compounds with superoxide. For example, the reaction of monosubstituted hydrazines (entries 1–5, Table I) with superoxide results in their overall conversion to nitrogen-free products. The fact that the autoxidation of monosubstituted hydrazines results in the same products[2-4] suggests that both processes may be proceeding through a similar mechanistic sequence.

1,2-Disubstituted *aryl*hydrazines and certain related hydrazo compounds (entries 6, 7, and 11) react with superoxide to produce the corresponding azo compound. By comparison, 1,2-disubstituted *dialkyl*hydrazines (as suggested by entry 8) are unaffected by treatment with superoxide under these conditions.[6] In contrast, treatment of several 1,1-disubstituted hydrazines (entries 9 and 10) with superoxide produced, inter alia, significant yields of the corresponding *N*-nitroso amine.

Finally, we have observed that superoxide reacts with certain hydrazones. Thus, a comparison of entries reveals that the hydrazones of acetophenone, benzophenone, and fluorenone (and by extension those of other *aryl* ketones and aldehydes) are converted by treatment with superoxide into the corresponding azine in high yield. However, the hydrazone of a simple representative *alkyl* ketone, viz., cyclohexanone, is unaffected by similar treatment with superoxide (cf. entry

15).[6] The fact that azines are the principal side product produced in the oxidation of unsubstituted hydrazones to diazoalkanes by such agents as mercury(II),[7] silver(I),[8] or manganese(IV) oxide[9] prompted us to briefly examine the reaction of several diazoalkanes with superoxide. Diphenyldiazomethane was recovered unchanged after treatment with superoxide. By comparison, the reaction of superoxide with diazofluorene produces fluorenone in high yield. The reason for this difference in reactivity is not obvious.

Our understanding of the detailed course of these reactions is still incomplete; however, several observations concerning the reaction of monosubstituted aryl hydrazines permit a description of the general features of its reaction with superoxide. First, oxidation of phenylhydrazine in benzene-d_6 produced biphenyl-d_5 (16%), and no observable biphenyl-d_0 or -d_{10} equivalent; benzene isolated from the oxidation of phenylhydrazine in toluene-d_8 showed no deuterium incorporation. Second, oxidation of a 1:1 mixture of 4-methylphenyl- and 4-chlorophenylhydrazine in benzene yielded only two coupling products: 4-methylbiphenyl (10%) and 4-chlorobiphenyl (12%). No other biphenyls were observed. Third, the reaction of 4-chlorophenylhydrazine with potassium superoxide in chlorobenzene produced the following mixture of coupling products: 2,4′-dichlorobiphenyl (8%), 3,4′-dichlorobiphenyl (4%), and 4,4′-dichlorobiphenyl (trace). Finally, the analogous oxidation of 4-methylphenylhydrazine in chlorobenzene yielded 2-chloro-4′-methylbiphenyl (9%), 3-chloro-4′-methylbiphenyl (4%), and 4-chloro-4′-methylbiphenyl (0.5%). Again, no other biphenyls were observed. These results are consistent with the intermediacy of free phenyl radicals in the oxidation of phenyl hydrazines by superoxide. Specifically, (i) the observed coupling products are all solvent derived and (ii) the relative biphenyl isomer distributions produced in chlorobenzene parallel those observed in established phenylation reactions.[10] In light of these arguments, a reasonable mechanism for the reaction of *aryl*hydrazines with superoxide would seem to involve its initial oxidation by superoxide to an aryldiazene (diimide) by an as yet undetermined pathway (eq 1).[11] Autoxidation of diazenes is rapid.[2,12] The subsequent oxidation of this intermediate by a radical chain reaction, in which the initial generation of a phenyl radical by a process whose precise nature need not be specified in detail (eq 2), would be followed by a hydrogen atom transfer from diazene followed by the unimolecular decomposition of the resulting arylazo radical (eq 3–4) to aryl radical and nitrogen. Attack of the aryl radical on the aromatic solvent (eq 5) leads to the observed coupling products.

$$\mathrm{ArNHNH_2} \xrightarrow{\mathrm{O_2^-}} \mathrm{ArN{=}NH} \qquad (1)$$

$$\mathrm{ArN{=}NH} \rightarrow \mathrm{Ar}\cdot \qquad (2)$$

$$\mathrm{Ar}\cdot + \mathrm{ArN{=}NH} \rightarrow \mathrm{ArH} + \mathrm{ArN{=}N}\cdot \qquad (3)$$

$$\mathrm{ArN{=}N}\cdot \rightarrow \mathrm{Ar}\cdot + \mathrm{N_2} \qquad (4)$$

$$\mathrm{Ar}\cdot + \mathrm{Ar'H} \rightarrow [\mathrm{Ar{-}Ar'H}]\cdot \xrightarrow{\mathrm{S}\cdot} \mathrm{Ar{-}Ar'} + \mathrm{SH} \qquad (5)$$

The significance of the observations described here is twofold. First, accepting the limitations on the generality of the reaction, the oxidation of arylhydrazines by superoxide provides a convenient nonphotochemical method for generating free aryl radicals at low temperatures under mild condition. As such, the reaction merits further development as a probe for the study of radical reactions. Second, hydrazo and related azo and azoxy compounds are concerned with a number of important biological reactions[4] including, for example, carcinogenesis[13] and monoamine oxidase inhibitation.[14] In view of the ubiquitous nature of superoxide in aerobic organisms, the results presented here may also provide some insight into the possible metabolic reactions of hydrazo compounds.

Further observations relevant to the mechanisms of these reactions will be reported in later papers.

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References and Notes

(1) Supported by the National Institutes of Health (AM-18713-01).
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(6) A substantial fraction (>90%) of this substrate and potassium superoxide were recovered unreacted after several days of mixing. The failure to observe an appreciable reaction between 1,2-di-*n*-butylhydrazine or cyclohexylhydrazone and superoxide may reflect the fact that the pK_a of alkylhydrazines and -hydrazones is significantly higher than that of arylhydrazines and -hydrazones (cf. P. A. S. Smith, "Open-Chain Nitrogen Compounds", Vol. II, W. A. Benjamin, New York, N.Y., 1966, pp 150, 151). If, as this observation suggests, the ability of O_2^- to effect the oxidation of these substrates is related to their acidity, it follows that proton abstraction is a necessary step in the oxidation of these substances by superoxide.
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New Photochromic Oxiranes. A Potential Precursor for 2,3-Diphenyloxirene

Summary. A pair of heterobicyclic oxides has been synthesized which undergoes photolysis to give stable cyclic carbonyl ylides; these ylides are highly colored, stable in the solid state as well as in fluid solution at low temperature, and bleach upon exposure to visible light; the photochemistry of epoxydiphenylmaleic anhydride in solution is described.

Sir: The thermal[1] and photoinduced[2] interconversion of three-membered heterocycles into singlet and triplet heterotrimethylene systems or ylides has evoked widespread theoretical[3] and synthetic interest.[1c–e,2] It has been established that stabilization of carbonyl ylides may be achieved by in-