nm (ϵ 1600), 298 (800); NMR ($CDCl_3$) δ 4.50 (s, 2 H), 7.3–7.8 (m, 4 H); IR (KBr) 1165, 1315 cm^{-1}.

5,5-Dideuteriopropanesultam. A solution containing propanesultam (0.7 g, 0.0058 mol), sodium carbonate (1.23 g, 0.012 mol), and D_2O (9 mL) was refluxed for 18 h. The solution was cooled, and acidified until pH 2 with 5 N DCl, and extracted five times with 10 mL of dichloromethane. The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. This afforded a colorless oil (0.47 g, 66%) which was purified by Kugelrohr distillation (120 °C, 0.02 mm): NMR ($CDCl_3$) δ 2.4 (t, 2 H), 3.38 (t, 2 H), 4.8 (br s, 1 H); IR (neat) 3350, 2500, 1310, 1160 cm^{-1}; MS, m/e (relative intensity) 123 (M^+, 100); exact mass calcd for $C_3D_2H_5NO_2S$ 123.031, found 123.032.

3-Isopropyl-1,2-benzisothiazole 1,1-dioxide was obtained as one of the decomposition products of *N*-bromo-3,3-diisopropyl-1,2-benzisothiazoline 1,1-dioxide: NMR ($CDCl_3$) δ 1.40 (d, 6 H), 3.38 (heptet, 1 H), 7.52–7.97 (m, 4 H); IR (KBr) 2970, 1560, 1340, 1170, 810 cm^{-1}; exact mass calcd for $C_{10}H_{11}NO_2S$ 209.051, found 209.050.

3-Alkyl-1,2-benzisothiazoline 1,1-Dioxides. In a typical example, sodium borohydride (0.17 g, 0.0045 mol) was added in small portions to a stirred solution of the appropriate thiazole (0.0011 mol) in anhydrous ether (30 mL). Then ethanol (20 mL) was added, and the resulting solution was stirred for 24 h at room temperature. After addition of 4 N HCl (3 mL) the organic solvents were removed in vacuo, and, after addition of chloroform (15 mL), the mixture was further hydrolyzed with 4 N HCl until pH 2. The organic layer was separated, and the aqueous layer was extracted with two portions of chloroform (15 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by crystallization and/or preparative layer chromatography (PLC).

3-Methyl-1,2-benzisothiazoline 1,1-Dioxide. After purification by PLC (SiO_2, ether) this compound was obtained in a yield of 40% as a colorless oil, which crystallized very slowly: NMR ($CDCl_3$) δ 1.55 (d, 3 H), 4.73 (m, 1 H), 5.25 (br s, 1 H), 7.2–7.8 (m, 4 H); IR (neat) 3300, 1295, 1170, 760 cm^{-1}; exact mass calcd for $C_8H_9NO_2S$ 182.966, found 182.965.

3-*n*-Butyl-1,2-benzisothiazoline 1,1-Dioxide. This compound was purified by PLC (SiO_2, ether) and recrystallized from 1:4 (v/v) benzene–*n*-hexane: yield 75%; mp 63–64 °C; NMR ($CDCl_3$) δ 0.65–2.20 (m, 9 H), 4.65 (dd, 1 H) 5.27 (d, 1 H) 7.2–7.8 (m, 4 H); IR (neat) 3300, 2960, 1480, 1400, 1300, 1175, 1140, 765 cm^{-1}; exact mass calcd for $C_{11}H_{15}NO_2S$ 225.082, found 225.083.

3-Isopropyl-1,2-benzisothiazoline 1,1-Dioxide. Obtained as a colorless oil: yield 67% [from 1:3 (v/v) benzene–*n*-hexane]; NMR ($CDCl_3$) δ 0.75 (d, 3 H), 1.10 (d, 3 H), 2.0–2.5 (m, 1 H), 4.65 (dd, 1 H), 5.35 (br d, 1 H), 7.2–7.85 (m, 4 H); IR (neat) 3300, 2970, 1480, 1300, 1170, 765 cm^{-1}; exact mass calcd for $C_{10}H_{13}NO_2S$ 211.067, found 211.068.

3-Cyclopentyl-1,2-benzisothiazoline 1,1-Dioxide. This compound was obtained during an attempt to synthesize the corresponding dicyclopentyl system by following the route of Mustafa.[28] Purification of the yellow oil by acid–base separation, column chromatography (neutral Al_2O_3, ether, R_f ~0.6; the column was eluted with an increasing amount of ethyl acetate) and crystallization from benzene–petroleum ether (60:80) afforded the product in low yield (6%): mp 82–84 °C; NMR ($CDCl_3$) δ 1.1–2.6 (m, 9 H), 4.62 (dd, 1 H), 5.05 (br s, 1 H), 7.1–7.8 (m, 4 H); IR (KBr) 3300, 2960, 1460, 1400, 1290, 1170, 760 cm^{-1}; MS, m/e (relative intensity) 237 (M^+), 168 ($M^+ - C_5H_9$, 100). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.37; H, 6.37; N, 5.90. Found: C, 60.18; H, 6.56; N, 5.73. The remaining N-brominations and N-chlorinations were carried out by following the method given for 2-bromo-3,3-dimethylethanesultam and *N*-chlorobenzyl sultam, respectively, except for *N*-chloro-3,3-dimethylethanesultam, which was prepared in the same way as *N*-chloroethanesultam.

Acknowledgment. We thank Dr. E. M. G. A. van Kruchten for technical assistance with the high-vacuum technique.

Registry No. **1**, 84108-76-9; **2**, 84108-77-0; **3a**, 74387-90-9; **3b**, 84108-78-1; **4**, 84108-79-2; **5**, 76826-98-7; **6**, 84108-81-6; **7**, 84108-82-7; **8a**, 84108-83-8; **8b**, 84108-84-9; **9**, 84108-85-0; **10**, 84117-44-2; **11**, 84108-86-1; **12**, 84108-87-2; **13**, 84108-88-3; $CH_3SO_2\dot{N}CH_3$, 74387-87-4; *o*-$MeC_6H_4SO_2\dot{N}CH_3$, 84108-80-5; $CH_3SO_2N(\dot{O})CH_3$, 27653-90-3; $C_6H_5SO_2N(\dot{O})CH_3$, 84109-02-4; *tert*-butyl hypochlorite, 507-40-4; ethanesultam, 34817-61-3; *N*-chloroethanesultam, 84108-89-4; 2-amino-2-methylpropane-1-thiol, 13893-24-8; 2-amino-2-methylpropanesulfonyl chloride hydrochloride, 84108-90-7; *tert*-butyl hypobromite, 1611-82-1; 3,3-dimethylethanesultam, 84108-91-8; *N*-bromo-3,3-dimethylethanesultam, 84108-92-9; 2,3-dihydro-1,2-benzisothiazole 1,1-dioxide, 936-16-3; pseudosaccharin chloride, 567-19-1; *N*-chloro-2,3-dihydro-1,2-benzisothiazole 1,1-dioxide, 84108-93-0; *N*-bromo-2,3-dihydro-1,2-benzisothiazole 1,1-dioxide, 84108-94-1; propanesultam, 5908-62-3; 5,5-dideuteriopropanesultam, 84108-95-2; *N*-bromo-3,3-diisopropyl-1,2-benzisothiazoline 1,1-dioxide, 84108-96-3; 3-isopropyl-1,2-benzisothiazole 1,1-dioxide, 84108-97-4; 3-methyl-1,2-benzisothiazoline 1,1-dioxide, 84108-98-5; 3-*n*-butyl-1,2-benzisothiazoline 1,1-dioxide, 84108-99-6; 3-isopropyl-1,2-benzisothiazoline 1,1-dioxide, 84109-00-2; 3-cyclopentyl-1,2-benzisothiazoline 1,1-dioxide, 84109-01-3.

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Quenching of Singlet Oxygen by 1,3,5-Triaryl-2-pyrazolines

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Received April 26, 1982

The efficient quenching of photochemically generated singlet oxygen by four 1,3,5-triaryl-2-pyrazolines (**5**–**8**) and *p*-(diethylamino)benzaldehyde diphenylhydrazone (**9**) has been investigated by inhibition of the photosensitized oxygenation of 1,3-diphenylisobenzofuran and 2-methyl-2-pentene. 1-Phenyl-3-[*p*-(diethylamino)styryl]-5-[*p*-(diethylamino)phenyl]-2-pyrazoline (**8**) quenches singlet oxygen without any reaction at all, and the quenching rate constant reaches a maximum of 5.8×10^9 M^{-1} s^{-1}. The quenching ability correlates with the value of their one-electron oxidation potentials (E_p).

It is well-known that singlet oxygen is an active oxygen species and that it may be involved in photodegradation of cells by pigments, light, and oxygen in biological systems.[1] Efficient quenchers of $^1O_2$[2] might, therefore, have practical importance. Carotenes,[3] the most efficient quenchers, show protective action against photobleaching

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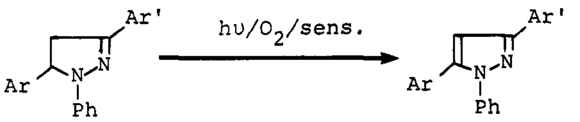
[1] (a) Foote, C. S. "Free Radical in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976; p 85. (b) Bellus, D. "Singlet Oxygen, Reactions with Organic Compounds and Polymers"; Rånby, B., Rabek, J. F., Eds.; Wiley: New York, 1978; p 61.

[2] For reviews see: (a) Foote, C. S. "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 139. (b) Ogryzlo, E. A., ref 1b, p 17. Young, R. H.; Brewer, D. R., ref 1b, p 36. Garner, A.; Wilkinson, F., ref 1b, p 48.

[3] (a) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 6233. (b) Foote, C. S.; Young, Y. C.; Denny, R. W. *Ibid.* **1970**, *92*, 5216, 5218.

0022-3263/83/1948-0542$01.50/0

Scheme I



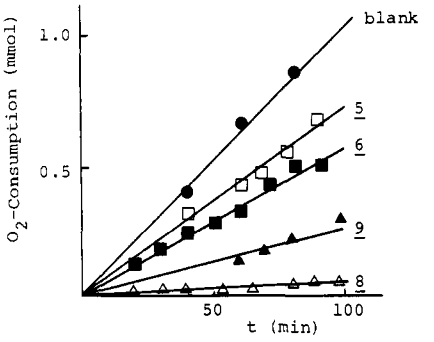


Figure 1. Photosensitized oxygenation of diethyl sulfide in the presence of 2-pyrazolines.

of chlorophyll *a*, but are not very stable to oxidation. Several tertiary aliphatic amines are capable of inhibiting oxidations by $^1O_2$,[4] and Dabco (1,4-diazabicyclo[2.2.2]octane)[5] is often used as a convenient quencher in photosensitized oxygenations, but the quenching rates appear to be somewhat lower than those for other quenchers.

Direct irradiation[6,7] and the dye-sensitized photooxidation[8] of various aryl-substituted 1,3-diphenyl-2-pyrazolines led to dehydrogenation to the corresponding pyrazoles. We have investigated the photosensitized oxidation of 1-phenyl-3,5-bis[para-substituted phenyl (or styryl)]-2-pyrazolines to clarify the substituent effect on oxidation by $^1O_2$ and found that some of them are extremely stable but capable of quenching $^1O_2$ efficiently.

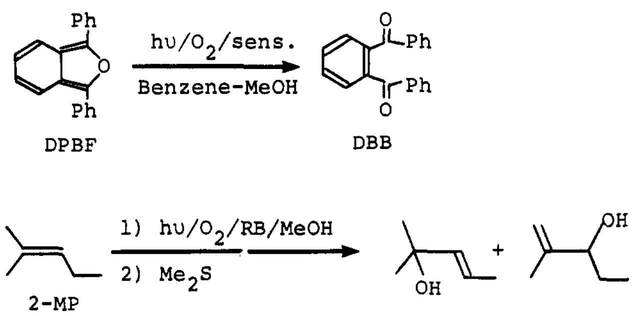
We now report here a new type of efficient $^1O_2$ quencher, 1,3,5-triaryl-2-pyrazolines (**5**–**8**) and the hydrazone (**9**) as a comparable compound to 2-pyrazolines, which quench $^1O_2$ generated in photosensitized oxidation remarkably well.

Results and Discussion

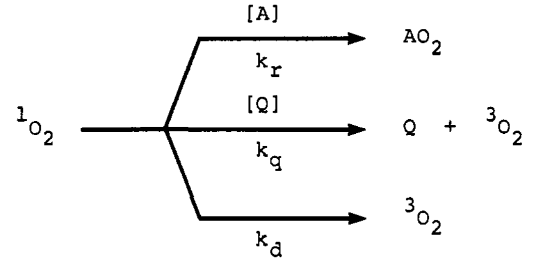
1,3,5-Triaryl-2-pyrazolines **1**–**6** were oxidized with photochemically generated $^1O_2$ to afford the corresponding pyrazoles (Scheme I). The relative rates of the photosensitized oxidation of 2-pyrazolines (Table I) seem to be reflected their oxidation potentials (E_p), which may suggest that 2-pyrazolines with low oxidation potentials can quench $^1O_2$ in the photosensitized oxidation. This might be supported by the fact that 1-phenyl-3-[*p*-(dimethylamino)phenyl]-2-pyrazoline (**7**, E_p = 0.49 V) and the 3-[*p*-(diethylamino)phenyl] derivative (**8**, E_p = 0.47 V) were not oxidized at all on prolonged irradiation.

As preliminary quenching experiments, Rose bengal (RB) photosensitized oxygenation of 1.6 × 10^{-2} M of diethyl sulfide ($k_r = 7 \times 10^6$ M^{-1} s^{-1}[9]) in chloroform–methanol (5:1) was carried out in the presence of 1.1 × 10^{-3} M of **5**, **6**, **8**, and **9**, and the results obtained are shown in Figure 1. Inspection of the data shown in Figure 1 indicates that oxygen absorption was apparently decreased by **8** and **9**. This suggests that $^1O_2$ was quenched very effectively by **8** and **9** at a rate on the order of 10^9 M^{-1} s^{-1}. These findings encouraged us to carry out an exploratory

Scheme II



Scheme III



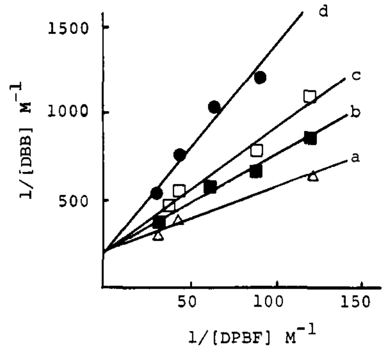


Figure 2. Photosensitized oxygenation of DPBF quenched by **8**. Concentration of added **8**: a, none; b, 1.3 × 10^{-3} M; c, 2.7 × 10^{-3} M; d, 5.4 × 10^{-3} M.

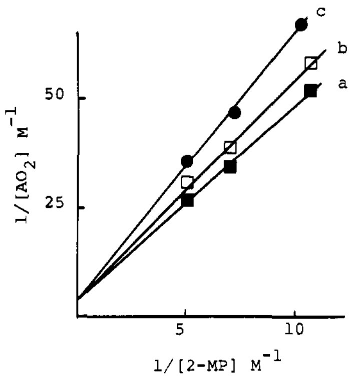


Figure 3. Photosensitized oxygenation of 2-MP quenched by **7**. Concentration of added **7**: a, none; b, 1.1 × 10^{-3} M; c, 2.1 × 10^{-3} M.

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[4] (a) Ogryzlo, E. A.; Tang, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 5034. Young; R. H.; Martin, R. L. *Ibid.* **1972**, *94*, 5183. (b) Matheson, I. B. C.; Lee, J. *Ibid.* **1972**, *94*, 3310. Furukawa, K.; Ogryzlo, E. A. *J. Photochem.* **1972**, *1*, 163. Young, R. H.; Martin, R. L.; Feriozi, D.; Brewer, D.; Kayser, R. *Photochem. Photobiol.* **1973**, *17*, 233. Monroe, B. M. *J. Phy. Chem.* **1977**, *81*, 1861.

[5] Quannes, C.; Wilson, T. *J. Am. Chem Soc.* **1968**, *90*, 6527.

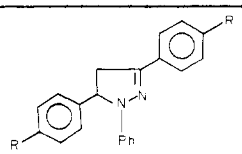
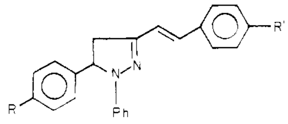
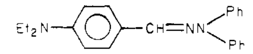
[6] Schrader, L. *Tetrahedron Lett.* **1971**, 2977.

[7] Evans, N. A.; Rivett, D. E.; Wilshire, J. F. K. *Aust. J. Chem.* **1974**, *27*, 2267.

[8] (a) Evans, N. A.; Leaver, I. H. *Aust. J. Chem.* **1974**, *27*, 1797. (b) Evans, N. A. *Aust. J. Chem.* **1975**, *28*, 433.

[9] Foote, C. S.; Peters, J. W. *Proc. 23rd Inst. Congr. Pure Appl. Chem., Spec. Lect.* **1971**, *4*, 129, cited in ref 1a.

Table I. Relative Rates of Photosensitized Oxidation of 1,3,5-Triaryl-2-pyrazolines

2-pyrazolines	no.	rel rates	E_p vs. SCE,[a] V
	1, R = H	15.4	0.89
	2, R = Me	9.8	0.83
	3, R = OMe	5.5	0.79
	4, R′ = Cl	7.3	0.89
	5, R′ = H	6.5	0.85
	6, R′ = OMe	1.0	0.76
	7, R′ = NMe_2	no reaction	0.49
	8, R′ = NEt_2	no reaction	0.47
	9	no reaction	0.56

[a] Oxidation potentials listed indicate the first peak potentials of the pyrazolines and hydrazone.

Table II. Kinetic Parameters Determined in Quenching Experiments

	DPBF		2-MP	
quenchers	k_q/k_r[a]	k_q,[b] M^{-1} s^{-1}	k_q/k_r[a]	k_q,[c] M^{-1} s^{-1}
5	0.27	1.7×10^8 (2.7×10^8)	890	7.2×10^8 (5.5×10^8)
6	2.0	1.3×10^9 (2.0×10^9)	740	6.0×10^8 (4.6×10^8)
7			2300	1.9×10^9 (1.4×10^9)
8	9.2	5.8×10^9 (9.2×10^9)		
9	1.4	8.8×10^8 (1.4×10^9)	2200	1.8×10^9 (1.4×10^9)

[a] $k_d = 1.8 \times 10^5$ s^{-1} was used for methanol.[13] [b] Determined by the photosensitized oxygenation of DPBF. k_q was calculated from the value 6.3×10^8 M^{-1} s^{-1} for k_r of DPBF.[14] Values in parentheses are k_q calculated from the value $k_r = 1.0 \times 10^9$ M^{-1} s^{-1} in methanol.[14] [c] Determined by the photosensitized oxygenation of 2-MP. k_r was taken to be 8.1×10^5 M^{-1} s^{-1}.[14] Values in parentheses are k_q calculated from the value $k_r = 6.2 \times 10^5$ M^{-1} s^{-1} in methanol.[14]

quenching experiment of $^1O_2$. The quenching efficiencies of 2-pyrazolines **5–8** and the hydrazone **9** were determined by measuring the inhibition rate for the reaction of $^1O_2$ with 1,3-diphenylisobenzofuran (DPBF),[10] which is known as one of the most reactive compounds toward $^1O_2$, and in addition with 2-methyl-2-pentene (2-MP).[11] Quenching rate constants were determined kinetically by the Zweig and Henderson modification[12] of the Foote method[2a)] (see Experimental Section). Conversions of the substrate were kept to less than 10%. Under the reaction conditions, 2-pyrazolines **5–8** and the hydrazone **9** were not oxidized appreciably. After irradiation, DPBF gave a sole product, o-dibenzoylbenzene (DBB), which was analyzed directly by gas chromatography (Scheme II). In the case of 2-MP, the amounts of hydroperoxides formed in photooxygenation were determined by gas chromatography after the reduction of alcohols with an excess amount of dimethyl sulfide. Results for photosensitized oxygenation of DPBF in the presence of **8** and of 2-MP in the presence of **7** are shown in Figures 2 and 3, respectively. Scheme III holds for photooxygenation of a substrate A in the presence of quencher, Q, where k_d, k_q, and k_r are the decay rate constants of $^1O_2$, the quenching rate constant by the quencher, and the reaction rate constant with the acceptor, respectively. $[^1O_2]$ is the total amount of $^1O_2$ generated in the reaction time. The steady-state kinetic equation for the formation of product AO_2 is given by

$$1/[AO_2] = 1/[^1O_2] + ((k_q[Q] + k_d)/k_r)(1/[^1O_2])(1/[A])$$

Table III. Quenching Rate Constants (k_q) of Several Quenchers[15]

quenchers	k_q, M^{-1} s^{-1}
8	5.8×10^9 (9.2×10^9)
β-carotene	above 10^{10}
Ni(II) chelate	above 10^{10}
aromatic amines	approachs 10^9
secondary and tertiary aliphatic amines	$(1\text{-}100) \times 10^6$
Dabco	above 10^7

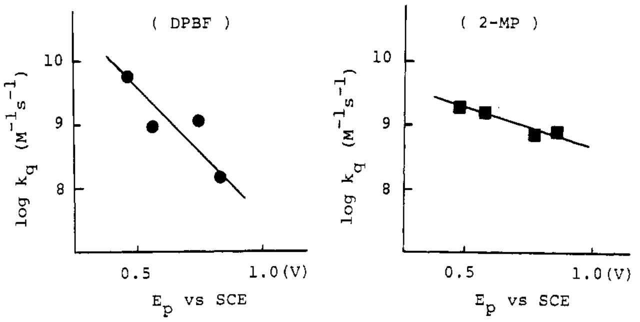


Figure 4. Relationship between one-electron oxidation potentials (E_p) and log k_q.

The best fit of the data gives k_q/k_r = 0.27, 2.0, 9.2, and 1.4 for the photosensitized oxygenation of DPBF in the presence of **5**, **6**, **8**, and **9**, respectively. These values depend critically on the value of intercepts of each of the lines as shown in Figure 2. We assume that quenching of the excited sensitizer by the quencher (**5**, **6**, **8**, and **9**) was not involved in the reaction. If such a process is involved, the only parameter in the equation that will be affected is $[^1O_2]$, which decreases with increasing concentration of the quencher. As a result, the intercepts were apparently constant. If only $^1O_2$ quenching is involved, the intercept of the plot does not change. Similar kinetic treatment for Figure 3 gave the quenching rate constants of $^1O_2$ for

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[10] Wilson, T. J. Am. Chem. Soc. 1966, 88, 2898.

[11] Foote, C. S. Acc. Chem. Res. 1968, 1, 104.

[12] Zweig, A.; Henderson, W. A. J. Polym. Sci., Polym. Chem. Ed. 1975, 13, 717.

[13] Young, R. H.; Wehrly, K.; Martin, R. L. J. Am. Chem. Soc. 1971, 93, 5774.

[14] Wilkinson, F.; Brummer, J. G. J. Phy. Chem. Ref. Data 1981, 10, 809.

[15] Foote, C. S., ref 2a, references cited therein.

photosensitized oxygenation of 2-MP. The quenching rate constants obtained are summarized in Table II. As shown in Tables II and III, these k_q values are remarkably large compared with those of other known $^1O_2$ quenchers and are comparable to the rate constant of β-carotene.[2] 2-Pyrazolines with relatively low oxidation potentials are stable under the reaction conditions and could act as good quenchers of $^1O_2$ as shown in Figure 4. This trend is similar to that the quenching ability of $^1O_2$ by tertiary amines which correlates with their ionization potentials.[4] It seems that an attractive mechanism for the quenching of $^1O_2$ by 2-pyrazoline and hydrazone derivatives would involve a charge-transfer process or weak molecular complexes, because all of them have relatively high electron densities on their rings as supported by their low oxidation potentials. Similar process are well-known in the quenching of $^1O_2$ by electron-rich compounds like amines.[2,4]

Experimental Section

Melting points are uncorrected. IR spectra were recorded with a Hitachi 26-50 spectrometer, NMR spectra with a Varian EM 360A spectrometer (solvent, deuteriochloroform; tetramethylsilane as an internal standard), and UV spectra with a Shimazu UV365 spectrometer. Cyclic voltammograms of substrates were obtained in 0.1 M n-Bu_4NClO_4/CH_3CN solution (vs. SCE; scan rate, 200 mV/s; Hokuto Denko Ltd., potentiostat/galvanostat Model HA-301). The one-electron oxidation potentials (E_p) obtained are listed in Table I. The light source was a xenon lamp (>440 nm) with a filter. Irradiations were carried out through a 2-mm slit in an ice–water bath while oxygen was passed through.

Diphenylisobenzofuran (DPBF, Tokyo Kasei) was used as received. Its purity was confirmed by the lack of a carbonyl absorption in the IR spectrum, and GLC analysis showed that no traces of o-dibenzoylbenzene (DBB) were contained in it. 2-Methyl-2-pentene (2-MP, Wako Pure Chemicals) was distilled from sodium hydride to remove alcoholic impurities, and its purity was confirmed by GLC analysis.

2-Pyrazolines[16] 1–8 and hydrazone[17] 9 were prepared from the corresponding ketones and hydrazines as previously reported. Pyrazoles were prepared from the oxidation of the corresponding 2-pyrazolines with lead tetraacetate.[17] The physical properties of the 2-pyrazolines, pyrazoles, and hydrazone prepared are as follows.

1: mp 135–136 °C (lit.[16] mp 133–135 °C); IR (KBr) 1595, 1490, 1390, 1320, 760, 740, 700, 695 cm^{-1}; UV λ_{max} 355 nm (log ϵ 4.25), 241 (4.15); ^{1}H NMR δ 3.08 (dd, 1 H, J = 7.2, 17.1 Hz), 3.84 (dd, 1 H, J = 12.3, 17.1 Hz), 5.29 (dd, 1 H, J = 7.2, 12.3 Hz), 7.03–7.94 (m, 15 H). Anal. Calcd for $C_{21}H_{18}N_2$: C,84.53; H,6.08; N,9.36. Found: C,84.46; H,6.04; N,9.35.

2: mp 143–145 °C; IR (KBr) 3030, 2900, 1595, 1490, 1380, 1320, 815, 740, 690 cm^{-1}; UV λ_{max} 354 nm (log ϵ 4.29), 242 (4.24); ^{1}H NMR δ 2.30 (s, 3 H), 2.37 (s, 3 H), 3.07 (dd, 1 H, J = 7.2 17.4 Hz), 3.82 (dd, 1 H, J = 11.4, 17.4 Hz), 5.25 (dd, 1 H, J = 7.2, 11.4 Hz), 6.97–7.47 (m, 11 H), 7.71 (d, 2 H, J = 8.4 Hz). Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.62; H, 6.79; N, 8.58. Found: C, 84.36; H, 6.80; N, 8.50.

3: mp 139–140 °C; IR (KBr) 3000, 2950, 2825, 1585, 1490, 1380, 1240, 820, 720 cm^{-1}; UV λ_{max} 352 nm (log ϵ 4.32), 247 (4.24), 227 (4.28); ^{1}H NMR δ 3.01 (dd, 1 H, J = 7.8, 16.8 Hz), 3.74 (s, 3 H), 3.77 (dd, 1 H, J = 12.6, 16.8 Hz), 3.82 (s, 3 H), 5.16 (dd, 1 H, J = 7.8, 12.6 Hz), 6.66–7.42 (m, 11 H), 7.72 (d, 2 H, J = 8.4 Hz). Anal. Calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.18; N, 7.81. Found: C, 76.68; H, 6.19; N, 7.71.

4: mp 209–211 °C (lit.[18] mp 212 °C); IR (KBr) 1580, 1480, 1380, 1320, 1095, 1080, 955, 750 cm^{-1}; UV λ_{max} 384 nm (log ϵ 4.55), 263 (4. 28); ^{1}H NMR δ 2.92 (dd, 1 H, J = 7.2, 16.8 Hz), 3.71 (dd, 1 H, J = 12.0, 16.8 Hz), 5.27 (dd, 1 H, J = 7.2, 12.0 Hz), 6.33–7.56 (m, 15 H). Anal. Calcd for $C_{23}H_{18}N_2Cl_2$: C, 70.23; H, 4.61; N, 7.12. Found: C, 70.24; H, 4.58; N, 7.13.

5: mp 151–153 °C (lit.[16] 151–153 °C); IR (KBr) 1580, 1490, 1390, 1320, 950, 740 cm^{-1}; UV λ_{max} 379 nm (log ϵ 4.51), 260 (4.18); ^{1}H NMR δ 2.94 (dd, 1 H, J = 7.2, 16.8 Hz), 3.69 (dd, 1 H, J = 12.0, 16.8 Hz), 5.22 (dd, 1 H, J = 7.2, 12.0 Hz), 6.32–7.58 (m, 17 H). Anal. Calcd for $C_{23}H_{20}N_2$: C, 85.15; H, 6.21; N, 8.63. Found: C, 84.98; H, 6.20; N, 8.59.

6: mp 156.5–157.5 °C; IR (KBr) 1595, 1500, 1320, 1250, 1025, 950, 820, 750 cm^{-1}; UV λ_{max} 377 nm (log ϵ 4.46), 292 (4.04), 285 (4.05), 225 (4.26); ^{1}H NMR δ 2.82 (dd, 1 H, J = 7.2, 16.2 Hz), 3.64 (dd, 1 H, J = 12.0, 16.2 Hz), 3.74 (s, 3 H), 3.82 (s, 3 H), 5.14 (dd, 1 H, J = 7.2, 12.0 Hz), 6.54–7.56 (m, 15 H). Anal. Calcd for $C_{25}H_{24}N_2O_2$: C, 78.09; H, 6.29; N, 7.28. Found: C, 78.09; H, 6.29; N, 7.16.

7: mp 185–187 °C; IR (KBr) 3025, 2925, 2850, 2800, 1595, 1350, 1320, 945, 725 cm^{-1}; UV λ_{max} 398 nm (log ϵ 4.59), 322 (4.26), 262 (4.32); ^{1}H NMR δ 2.85 (s, 6 H), 2.96 (s, 6 H), 2.88 (dd, 1 H, J = 7.2, 16.8 Hz), 3.59 (dd, 1 H, J = 12.0, 16.8 Hz), 5.06 (dd, 1 H, J = 7.2, 12.0 Hz), 6.44–7.93 (m, 15 H). Anal. Calcd for $C_{27}H_{30}N_4$: C, 78.98; H, 7.36; N, 13.64. Found: C, 79.05; H, 7.37; N, 13.50.

8: mp 127–129 °C; IR (KBr) 3010, 2950, 2900, 2870, 1585, 1490, 1345, 1320, 940, 800, 740 cm^{-1}; UV λ_{max} 396 nm (log ϵ 4.66), 322 (4.08), 264 (4.37); ^{1}H NMR δ 1.13 (t, 6 H, J = 6.6 Hz), 2.77–3.90 (m, 10 H), 5.13 (dd, 1 H, J = 7.2, 11.4 Hz), 6.22–7.54 (m, 15 H). Anal. Calcd for $C_{31}H_{38}N_4$: C, 79.78; H, 8.20; N, 12.00. Found: C, 79.72; H, 8.18; N, 11.96.

9: mp 97–96 °C; IR (KBr) 3025, 2950, 2900, 2850, 1595, 1480, 1345, 810, 740, 690 cm^{-1}; UV λ_{max} 363 nm (log ϵ 4.52), 331 (4.33); ^{1}H NMR δ 1.16 (t, 6 H, J = 7.8 Hz), 3.38 (q, 4 H, J = 7.8 Hz), 6.70 (d, 2 H, J = 9.6 Hz), 7.12–7.70 (m, 13 H). Anal. Calcd for $C_{23}H_{25}N_3$: C, 80.42; H, 7.33; N, 12.23. Found: C, 80.51; H, 7.35; N, 12.25.

1,3,5-Triphenylpyrazole: mp 139–140 °C (lit.[8] mp 139–140 °C); IR (KBr) 1595, 1490, 1380, 1320, 830, 760, 695, 685 cm^{-1}; UV λ_{max} 252 nm (log ϵ 4.50); ^{1}H NMR δ 6.84 (s, 1 H), 7.19–7.58 (m, 13 H), 7.98 (m, 2 H). Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.10; H, 5.44; N, 9.45. Found: C, 85.10; H, 5.49; N, 9.26.

1-Phenyl-3,5-di-*p*-tolylpyrazole: mp 112–113 °C; IR (KBr) 3020, 2900, 1580, 1490, 1340, 820, 790, 760, 680 cm^{-1}; UV λ_{max} 254 nm (log ϵ 4.26); ^{1}H NMR δ 2.29 (s, 3 H), 2.36 (s, 3 H), 6.78 (s, 1 H), 7.06–7.48 (m, 11 H), 7.88 (d, 2 H, J = 9.0 Hz). Anal. Calcd for $C_{23}H_{20}N_2$: C, 85.15; H, 6.21; N, 8.63. Found: C, 85.04; H, 6.22; N, 8.64.

1-Phenyl-3,5-bis(*p*-methoxyphenyl)pyrazole: mp 158 °C; IR (KBr) 3030, 2990, 2950, 2920, 2810, 1600, 1480, 1250, 820, 790, 760 cm^{-1}; UV λ_{max} 264 nm (log ϵ 4.58); ^{1}H NMR δ 3.78 (s, 3 H), 3.84 (s, 3 H), 6.68–7.46 (m, 12 H), 7.90 (d, 2 H, J = 9.0 Hz). Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.50; H, 5.65; N, 7.85. Found: C, 77.40; H, 5.65; N, 7.85.

1-Phenyl-3-(*p*-chlorostyryl)-5-(*p*-chlorophenyl)pyrazole: mp 144.5–145.5 °C; IR (KBr) 1585, 1480, 1360, 1080, 960, 820, 800, 760, 690 cm^{-1}; UV λ_{max} 297 nm (log ϵ 4.54), 233 (4.30), 225 (4.32); ^{1}H NMR δ 6.72 (s, 1 H), 7.05–7.54 (m, 15 H). Anal. Calcd for $C_{23}H_{16}N_2Cl_2$: C, 70.59; H, 4.12; N, 7.15. Found: C, 70.50; H, 4.06; N, 7.13.

1,5-Diphenyl-3-styrylpyrazole: mp 138–139 °C (lit.[16] mp 141 °C); IR (KBr) 1580, 1480, 1360, 960, 760, 695 cm^{-1}; UV λ_{max} 298 nm (log ϵ 4.54), 231 (4.29), 224 (4.32); ^{1}H NMR δ 6.76 (s, 1 H), 7.14–7.70 (m, 17 H). Anal. Calcd for $C_{23}H_{18}N_2$: C, 85.68; H, 5.62; N, 8.68. Found: C, 85.47; H, 5.64; N, 8.66.

1-Phenyl-3-(*p*-methoxystyryl)-5-(*p*-methoxyphenyl)-pyrazole: mp 172.5–173.5 °C; IR (KBr) 1600, 1490, 1360, 1240, 1020, 960, 830, 760 cm^{-1}; UV λ_{max} 297 nm (log ϵ 4.60), 231 (4.21); ^{1}H NMR δ 3.80 (s, 3 H), 3.86 (s, 3 H), 6.70–8.72 (m, 16 H). Anal. Calcd for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.79; N, 7.32. Found: C, 78.44; H, 5.81; N, 7.31.

Photosensitized Oxidation of 2-Pyrazoline and Hydrazone Derivatives. Rate Measurements. As an example, a weighed amount of 2-pyrazoline dissolved in methylene chloride was irradiated by using methylene blue (MB) as a sensitizer. A constant volume of the solution was pipetted out at constant time intervals, and the optical density of the solution was measured at λ_{max} of 2-pyrazoline by UV spectrometer.

Compound 8 (1 mmol) was dissolved in 30 mL of chloroform and irradiated overnight with a 300-W halogen lamp while oxygen was passed through with MB as a sensitizer. 8 was recovered

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quantitatively, and none of the oxidized product was detected by NMR spectra and TLC analysis.

Quenching of Photosensitized Oxygenation of Diethyl Sulfide. A chloroform–methanol (5:1) solution of diethyl sulfide (1.6×10^{-2} M) and rose bengal (RB, 2.5×10^{-5} M) in the absence or presence of the quencher (1.1×10^{-3} M) was saturated with oxygen, and the system was closed and irradiated. At constant time intervals, the amount of absorbed oxygen was measured by using a buret in the closed system. The results obtained are shown in Figure 1.

Photosensitized Oxygenation of DPBF. Stock solution of RB (2 mL, 3.5×10^{-3} M) in methanol and 8 mL of freshly prepared DPBF with 2-pyrazoline or hydrazone (variable concentrations of DPBF to constant concentrations of 2-pyrazoline or hydrazone) in methanol–benzene (3:2) were mixed in Pyrex reaction tubes. After irradiation for a constant time (4 min) under oxygen bubbling, the internal standard, 9,10-diphenylanthracene (DPA), was added, and the reaction mixture was immediately analyzed by GLC. Analytical conditions were as follows: 4 mm × 1 m glass column, 10% SF-96 on Chromosorb, column temperature 200 °C; Hitachi 164 gas chromatograph with an FID detector. The yields of produced DBB were determined by comparison of the peak areas with that of the internal standard (DPA).

Photosensitized Oxygenation of 2-MP. For the determination of the product alcohols in RB-photosensitized oxygenation of 2-MP, gas chromatographic separation of the alcohols was carried out on an Ohkura gas chromatograph, Model 802 (6 mm × 1.5 m stainless steel column, 10% Carbowax 20M on Celite 545), after the photooxygenated mixture was reduced with an excess amount of dimethyl sulfide overnight. Two alcohols were separated, 4-methyl-2-penten-4-ol [oil; IR (NaCl) 3380 cm^{-1} (OH); ^{1}H NMR δ 5.53 (m, 2 H), 2.10 (br s, 1 H), 1.67 (d, 3 H, $J = 6.0$ Hz), 1.20 (s, 6 H)] and 2-methyl-1-penten-3-ol: oil; IR (NaCl) 3370 cm^{-1} (OH); ^{1}H NMR δ 4.80 (d, 2 H), 4.10 (t, 1 H, $J = 6.2$ Hz), 2.10 (s, 3 H), 1.63 (dq, 2 H, $J = 6.2, 7.0$ Hz), 1.20 (t, 3 H, $J = 7.0$ Hz).

Stock solution of RB (5 mL, 3.9×10^{-4} M) in methanol, 5 mL of freshly prepared 2-MP, and 5 mL of 2-pyrazoline or hydrazone (variable concentrations of 2-MP to constant concentrations of 2-pyrazoline or hydrazone) in methanol–benzene (3:2) were mixed in the Pyrex reaction tubes. After irradiation for a constant time (10 min), the reaction mixture was reduced with an excess of dimethyl sulfide and allowed to stand for 6 h, and the internal standard (cyclohexanone) was added to the reaction mixture and analyzed by GLC. Analytical conditions were as follows: 4 mm × 2 m glass column, 10% Carbowax 20M on Celite 545, column temperature 80 °C. The yields of alcohols were determined by the comparison of the peak areas with that of the internal standard.

Registry No. **1**, 742-01-8; **2**, 84237-85-4; **3**, 10180-07-1; **4**, 2256-22-6; **5**, 2515-62-0; **6**, 2256-18-0; **7**, 2564-18-3; **8**, 57609-72-0; **9**, 68189-23-1; RB, 11121-48-5; diethyl sulfide, 352-93-2; 1,3-diphenylisobenzofuran, 5471-63-6; 2-methyl-2-pentene, 625-27-4; O_2, 7782-44-7.

Chemistry of Higher Order, Mixed Organocuprates. 5.[1] On the Choice of the Copper(I) Salt for the Formation of R_2CuLi

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Chemical and spectroscopic studies are presented that have been designed to manifest differences in reagent composition and reactivity between mixtures of CuI/2RLi and CuSCN/2RLi. The results indicate that while both Cu(I) salts are reported to serve as precursors to lower order cuprates R_2CuLi, CuSCN may actually be forming a higher order, mixed species $R_2Cu(SCN)Li_2$. This would explain the discrepancy in coupling reactions of each solution with similar organic substrates under otherwise identical conditions. The presence of added lithium salts demonstrates that while LiI added to CuSCN/2RLi has essentially no effect, introduction of an equivalent of LiSCN to CuI/2RLi dramatically alters the efficiency of ligand transfer.

Introduction

Some 30 years ago, Gilman described[3] the first preparation of Me_2CuLi, **1**, an example of a class of organocopper compounds of general formula R_2CuLi that have come to be known as Gilman reagents. In this original report it was stated that either copper(I) halides or cuprous thiocyanate (CuSCN), upon addition of 2 equiv of MeLi in Et_2O, led to solutions of **1**. In the course of our studies on the nature[4] and synthetic potential[5] of higher order, mixed cuprates $R_2Cu(CN)Li_2$, **2**, it has been demonstrated not unexpectedly that in their preparation the Cu–CN moiety remained intact as shown by infrared spectroscopy. This lack of simple metal–metal exchange (i.e., $RLi + CuCN \nrightarrow RCu + LiCN$) may be attributed to the likelihood of $d\pi$ backbonding.[6] We were curious as to how a Cu(I) salt containing a related nontransferable ligand L [i.e., $R_2Cu(L)Li_2$, $L \neq CN$] would affect the reactions of higher order reagents relative to **2**. Thiocyanate was selected and led us to examine the possibility that the combination of 2RLi plus CuSCN might lead to a higher order species $R_2Cu(SCN)Li_2$, **3**, rather than a lower order Gilman cuprate. Herein we describe both chemical and spectroscopic data designed to elucidate the nature of the reagents so formed and point to the care that must be exercized in choosing a source of Cu(I) en route to the preparation of "R_2CuLi", **4**.

Results and Discussion

It was anticipated, should CuSCN lead to **3**, that a difference in chemical reactivity between a lower and

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