(analytical grade, 16–50 mesh, 1.99 mequiv of H/mL, 14 mequiv of H) in 10 mL of anhydrous ether was added 3.0 g (12.4 mmol) of 1-(trimethylsiloxy)-6-(trimethylsilyl)-5-hexyne (1). The reaction was monitored by GC analysis of 0.2-μL aliquots removed by syringe directly from the reaction mixture. After 19 h, the reaction was filtered through a coarse sintered-glass frit and the filtrate dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 2.12 g of an oil, which was shown by GC to contain 1.4% of starting material and 98.6% of 6-(trimethylsilyl)-5-hexyn-1-ol (2). The product can be used directly or purified by fractional distillation to yield 1.98 g (11.7 mmol, 94%) of pure (trimethylsilyl)alkynol: bp 55–56 °C (0.5 mmHg); IR (neat) 3425, 2180, 1250, 1050, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.68 (t, J = 6 Hz, 2 H), 2.28 (t, J = 6 Hz, 2 H), 1.82 (br s, 1 H), 1.66 (m, 4 H), 0.14 (s, 9 H); mass spectrum, m/z (relative intensity) 170 (M^+, 0.2), 75 (100), 73 (25.5); exact mass calcd for $C_9H_{18}OSi$ m/z 170.1127, found m/z 170.1099.

The above procedure was exactly the same for all the resins utilized in this study.

5-(Trimethylsilyl)-4-pentyn-1-ol (4):[2] bp 47–49 °C (0.5 mmHg); IR (neat) 3330, 2180, 1250, 1045, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.71 (t, J = 6 Hz, 2 H), 2.41 (br s, 1 H), 2.30 (t, J = 6 Hz, 2 H), 1.72 (quintet, J = 6 Hz, 2 H), 0.12 (s, 9 H); mass spectrum, m/z (relative intensity) 156 (M^+, 0.2), 125 (11), 99 (14), 75 (100), 73 (30); exact mass calcd for $C_8H_{16}OSi$ m/z 156.0970, found m/z 156.1010.

3-(Trimethylsilyl)-2-propyn-1-ol (6):[4] bp 51–52 °C (3 mmHg) [lit.[4] bp 71 °C (15 mmHg)]; IR (neat) 3350, 2180, 1250, 1040, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.16 (s, 2 H), 3.12 (br s, 1 H), 0.12 (s, 9 H); mass spectrum, m/z (relative intensity) 124 (M^+, 0.6), 85 (100), 75 (36), 73 (40); exact mass calcd for $C_6H_{12}OSi$ m/z 128.0657, found m/z 128.0695.

4-(Trimethylsilyl)-3-butyn-2-ol (8): bp 49–51 °C (1.5 mmHg); IR (neat) 3330, 2175, 1371, 1250, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.43 (q, J = 6 Hz, 1 H), 3.34 (br s, 1 H), 1.40 (d, J = 6 Hz, 3 H), 0.15 (s, 9 H); mass spectrum, m/z (relative intensity) 124 ($M^+ - H_2O$, 2), 99 (100), 75 (12), 73 (13); exact mass calcd for $C_7H_{14}OSi{\cdot}H_2O$ m/z 124.0709, found m/z 124.0665.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. D.V.H. is grateful for partial support in the form of an ACS-PRF Visiting Summer Faculty Fellowship during the summer of 1985. D.V.H. also acknowledges supplemental support from the Oklahoma State University Center for Energy Research as well as a grant from Southwestern Oklahoma State University. We are indebted to M. J. Fields for technical assistance in the preparation of one of the starting materials used in this study.

Photochemical Reactions of 2,4-Dinitro-6-phenyliodonium Phenolate with Alkenes, Alkynes, and Aromatic Compounds

Spyros P. Spyroudis

Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki 54006, Greece

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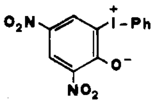
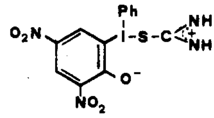
2,4-Dinitro-6-phenyliodonium phenolate, a stable iodonium zwitterion, reacts under photolytic conditions with various alkenes, alkynes, and aromatic compounds to afford 2,3-dihydrobenzo[*b*]furans, benzo[*b*]furans, and 6-aryl-2,4-dinitrophenols. A possible reaction pathway involving the intermediacy of hypervalent iodine compounds is proposed.

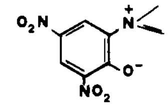
Zwitterionic iodonium compounds constitute an interesting class of hypervalent iodine compounds, the chemistry of which has recently been reviewed.[1] In our continuing exploration of the chemistry of hypervalent iodine compounds we have reported[2] the synthesis and reactivity of some 2-oxidodiaryliodonium zwitterions. Among them 2,4-dinitro-6-phenyliodonium phenolate (1) is easily prepared and fairly stable.[2] The phenyliodonio group in 1 can be displaced by basic nucleophiles,[2] whereas other nucleophiles react with 1 only under photolytic conditions. Thus irradiation of 1 in carbon disulfide affords 5,7-dinitro-1,3-benzoxathiole-2-thione.[3] Similarly phenyl isothiocyanate with 1 gives 5,7-dinitro-2-phenylimino-1,3-benzoxathiole.[4] Stable iodinanes 2 have been isolated from the photochemical reaction of 1 with various thioureas,[4] whereas pyridinium zwitterions 3 have been formed from the photoreaction of 1 with pyridines.[4]



1



2



3

The photochemical reaction of 1 with various alkenes, alkynes, and aromatic compounds are reported here.

Results and Discussion

When a suspension of 1 in acetonitrile was irradiated in the presence of an alkene 4 for several hours, 2,3-dihydrobenzo[*b*]furans 5 and/or 6-alkenyl-2,4-dinitrophenols 6 were isolated (Table I).

The above reaction provides an easy route to various 2,3-dihydrobenzo[*b*]furans, the synthesis of which has attracted much attention because of their interesting pharmacological properties.[5] An analogous reaction involving in situ generated carbenoid species has been described by Huisgen.[6] 2,3-dihydrobenzo[*b*]furans were

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[1] Koser, G. F. *The Chemistry of Functional Groups*; Wiley: New York, 1983; Supplement D, Chapter 18, pp 774–806.

[2] Spyroudis, S.; Varvoglis, A. *J. Chem. Soc. Perkin Trans.* **1984**, 135.

[3] Papadopoulou, M.; Spyroudis, S.; Varvoglis, A. *J. Org. Chem.* **1985**, *50*, 1509.

[4] Spyroudis, S. *Liebigs Ann. Chem.*, in press.

[5] Donnely, D.; Meegan, M. In *Comprehensive Heterocyclic Chemistry*; Pergamon: New York, 1984; Vol 4, Chapter 3.12, p 708.

[6] Binch, G.; Huisgen, R.; König, H. *Chem. Ber.* **1964**, *97*, 2893.

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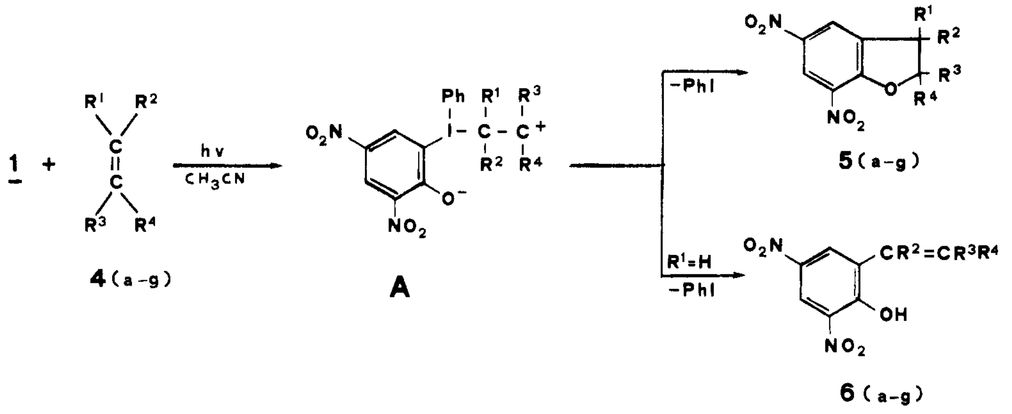
Table I. Photochemical Reactions of 1 with Alkenes



alkene	products			
	5		6	
		yield, %		yield, %
4a, $R^1 = R^3 = H$, $R^2,R^4 = (CH_2)_4$	5a	9	6a	24
4b, $R^1 = R^3 = H$, $R^2,R^4 =$ 	5b	0	6b	19
4c, $R^1 = R^2 = R^3 = R^4 = CH_3$	5c	30	6c	0
4d, $R^1 = R^2 = H$, $R^3 = R^4 = Ph$	5d	17	6d	24
4e, $R^1 = R^2 = R^3 = H$, $R^4 = Ph$	5e	22	6e	14[a]
4f, $R^1 = R^2 = R^3 = H$, $R^4 = OCOCH_3$	5f	38	6f	0
4g, $R^1 = R^2 = R^3 = H$, $R^4 = OCH_2CH(CH_3)_2$	5g	34	6g	0

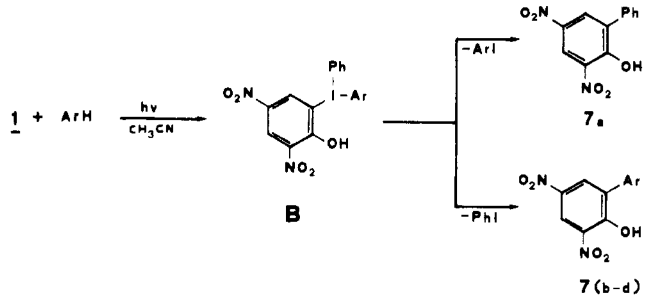
[a] 1:1 mixture of the cis–trans isomers.

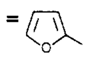
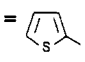
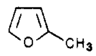
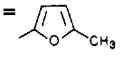
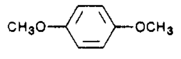
isolated from the thermal reaction of 3,4,5,6-tetrachloro-2-diazocyclohexa-3,5-dien-1-one with alkenes. The intermediacy of carbenes or carbenoid species in the photochemical reactions of 1 with alkenes seems unlikely since no Wolf-type rearrangement products were isolated from these reactions and irradiation of 1 alone in acetonitrile left it unchanged.

It is possible that the reaction of 1 with alkenes starts with the electrophilic attack of the positively charged iodine to the double bond. It must be noted that the reaction proceeds only photochemically at room temperature, since at higher temperatures only the rearrangement product, 6-iodo-2,4-dinitro-1-phenoxy-benzene,[2] was isolated. The intermediate iodinane of type A is very unstable and with the expulsion of iodobenzene either cyclizes to 5 or forms the phenol 6. The intermediacy of the iodinane A also explains the regioselectivity in the formation of both products. Iodinanes with three C–I bonds, specifically triaryl iodinanes, are known to exist but are unstable compounds[7,8] which easily decompose to the corresponding aryl iodides either heterolytically or homolytically.[9]

Some of the phenols 6 can be formed partly from the thermal rearrangement of the corresponding 2,3-dihydrobenzo[*b*]furans 5. Indeed compounds 5 have the tendency to isomerize to 6 upon heating, the most characteristic of all being the complete conversion of 5,7-dinitro-2-phenyl-2,3-dihydrobenzo[*b*]furan (5e) to *cis*-2,4-dinitro-(2-phenylethenyl)phenol (6e) at room temperature in 2 days. Since other 2,3-dihydrobenzo[*b*]furans, e.g., the analogous 4,5,6,7-tetrachloro-2-phenyl-2,3-dihydrobenzo-[*b*]furan, are reported[6] to be stable this rearrangement must be affected by the two nitro groups on the aromatic ring.

Table II. Photochemical Reactions of 1 with Aromatic Compounds



ArH	product	
		yield, %
PhH	7a	74
	7b, Ar = 	70
	7c, Ar = 	64
	7d, Ar = 	54
$PhOCH_3$	7a	76
	7a	69

The intermediate formation of iodinanes of type A is confirmed by the results of the photochemical reactions of 1 with aromatic compounds. When a suspension of 1 in acetonitrile was irradiated in the pesence of an aromatic compound the corresponding 6-aryl-2,4-dinitrophenols 7 a–d were isolated (Table II).

The triaryl iodinanes of type B are unstable under the conditions of the experiment and decompose to phenols 7 with the expulsion of iodobenzene or iodoarene in the case of activated rings. The reaction does not proceed with chlorobenzene and nitrobenzene, indicating that the iodine atom does not have a strong enough electrophilic character to attack these rings.

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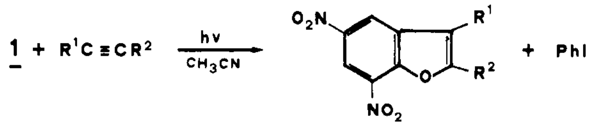
(7) Clauss, K. *Chem. Ber.* **1955**, *88*, 268.
(8) Reich, H.; Cooperman, C. *J. Am. Chem. Soc.* **1973**, *95*, 5077.
(9) Beringer, F.; Chang, L. *J. Org. Chem.* **1971**, *36*, 4055.

Table III. Photochemical Reactions of 1 with Alkynes



8(a-c)

R¹C≡CR²		product	
R¹	R²		yield, %
Ph	Ph	**8a**	30
$COOCH_2CH_3$	$COOCH_2CH_3$	**8b**	17
H	Ph	**8c**	18

When **1** was irradiated in the presence of an alkyne the corresponding benzo[*b*]furans **8** were formed (Table III).

The reaction must also proceed via the formation of unstable iodinanes. Similarly benzo[*b*]furans were formed from the 1,3-dipolar cycloaddition of carbenoid species, generated from 3,4,5,6-tetrachloro-2-diazocyclohexa-3,5-dien-1-one with alkynes.[10]

No photoreaction between **1** and nitriles such as propionitrile, pivalonitrile, and benzonitrile was observed.

Experimental Section

Melting points were determined on a Kofler hotstage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. UV spectra were recorded on a Shimadzu UV 210A spectrophotometer. ^{1}H NMR spectra were obtained with a Varian A-60A spectrometer. MS spectra were obtained with a Hitachi-Perkin-Elmer RMU-6L, single focusing (at 70 eV) instrument.

Irradiations were performed with a low-pressure Hg lamp (400 W, Pyrex vessel). **1** was obtained from the reaction of 2,4-dinitrophenol and bis(trifluoroacetoxy)iodobenzene.[2]

Photochemical Reactions of 1 with Alkenes. General Procedure. A suspension of **1** (386 mg, 1 mmol) in acetonitrile (20 mL) and the corresponding alkene (3–10 mL) was irradiated with continual stirring until the complete disappearance of **1** (4–10 h). After concentration the resulting solution was either directly chromatographed on column (silica gel, dichloromethane–hexane, 1:1 gradually increased to 3:1, as eluant) or chromatographed after the removal of the acidic compounds (washing with 10% NaOH). The phenols **6** were obtained after acidification of the alkaline solution by filtration and were chromatographed on column as previously. The two methods gave essentially the same results.

Iodobenzene and, in some cases, excess alkene were the first to be eluted.

Reaction with Cyclohexene. chromatographic separation afforded 63 mg (24% yield) of 2,4-dinitro-6-(cyclohexen-1-yl)phenol (**6a**): mp 89–90 °C (from hexane); UV λ_{max} 250 nm (ϵ 9000), 218 (12000); IR (Nujol mull) 3200 (br), 3100, 1610, 1550, 1340 cm^{-1}; ^{1}H NMR (CCl_4) δ 10.55 (1 H, br), 8.87 (1 H, d, J = 2 Hz), 8.28 (1 H, d, J = 2 Hz), 6.00 (1 H, m), 2.31–1.72 (8 H, m); MS, *m/e* (relative itensity) 264 (M$^+$, 50), 247 (100), 217 (40), 205 (20), 183 (10).

Anal. Calcd for $C_{12}H_{12}N_2O_5$: C, 54.54; H, 4.54; N, 10.60. Found: C, 54.54; H, 4.58; N, 10.75.

5,7-Dinitro-2,3-butano-2,3-dihydrobenzo[*b*]furan (**5a**) (24 mg; 9% yield) was also obtained: oil; UV λ_{max} 312 nm (ϵ 11300), 252 (14500), 218 (15700); IR (neat) 3100, 1620, 1540, 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.08 (1 H, d, J = 2 Hz), 8.43 (m, 1 H), 5.23–5.08 (1 H, m), 2.05–1.1 (9 H, m); MS, *m/e* (relative intensity) 264 (M$^+$, 100), 247 (95), 218 (32).

Anal. Calcd for $C_{12}H_{12}N_2O_5$: C, 54.54; H, 4.54; N, 10.60. Found: C, 54.55; H, 4.52; N, 10.42.

Reaction with Norbornylene. From this reaction only 2,4-dinitro-6-(norbonylen-1-yl)phenol (**6b**) (52 mg; 19% yield) was isolated: mp 100–101 °C (from hexane); UV λ_{max} 262 nm (ϵ 20400), 205 (6400); IR (Nujol mull) 3210 (br), 3090, 1610, 1540, 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.60 (1 H, br), 9.00 (1 H, d, J = 2 Hz), 8.57 (1 H, d, J = 2 Hz), 7.10 (1 H, m), 3.45 (1 H, m), 3.16 (1 H, m), 2.05–1.13 (6 H, m); MS, *m/e* (relative intensity) 276 (M$^+$, 16), 246 (100), 229 (24), 200 (91), 127 (35).

Anal. Calcd for $C_{13}N_{12}N_2O_5$: C, 56.52; H, 4.35; N, 10.14. Found: C, 56.50; H, 4.20; N, 10.12.

Reaction with Tetramethylethylene. 5,7-Dinitro-2,2,3,3-tetramethyl-2,3-dihydrobenzo[*b*]furan (**5c**) was the only product to be isolated (80 mg; 30% yield): mp 139–140 °C (from chloroform–hexane); UV λ_{max} 312 nm (ϵ 12500), 251 (15000), 218 (16000); IR (Nujol mull) 1610, 1530, 1330, 1110, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.78 (1 H, d, J = 2 Hz), 8.03 (1 H, d, J = 2 Hz), 1.48 (6 H, s), 1.32 (6 H, s); MS, *m/e* (relative intensity) 266 (M$^+$, 25), 251 (10), 208 (35), 191 (65), 162 (25), 83 (100).

Anal. Calcd for $C_{12}H_{14}N_2O_5$: C, 54.13; H, 5.26; N, 10.52. Found: C, 53.92; H, 5.18; N, 10.29.

Reaction with 1,1-Diphenylethylene. From this reaction 61 mg (17% yield) of 5,7-dinitro-2,2-diphenyl-2,3 dihydrobenzo[*b*]furan (**5d**) was isolated: mp 137–138 °C (needles from chloroform–hexane); UV λ_{max} 305 nm (ϵ 7400), 252 (9500), 206 (20600); IR (Nujol mull) 3100, 1610, 1550, 1340, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.04 (1 H, d, J = 2 Hz), 8.40 (1 H, m), 7.74–7.32 (10 H, m), 4.20 (2 H, m); MS, *m/e* (relative intensity) 362 (M$^+$, 95), 345 (100), 315 (44), 269 (15), 239 (22), 225 (45).

Anal. Calcd for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.87; N, 7.73. Found: C, 66.35; H, 3.83; N, 7.30.

2,4-Dinitro-6-(2,2-diphenylethenyl)phenol (**6d**) (87 mg; 24% yield) was also obtained: mp 119–120 °C (from hexane); IR (Nujol mull) 3230 (br), 3100, 1630, 1605, 1560, 1350, 1280, 1040, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.80 (1 H, br), 8.86 (1 H, d, J = 2 Hz), 7.91 (1 H, d, J = 2 Hz), 7.43–7.12 (11 H, m); MS, *m/e* (relative intensity) 362 (M$^+$, 100), 345 (94), 315 (52), 239 (36), 269 (15).

Anal. Calcd for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.87; N, 7.73. Found: C, 66.43; H, 3.70; N, 7.64.

Reaction with Styrene. From the alkaline solution an unseparable mixture of *cis*- and *trans*-2,4-dinitro-6-(2-phenylethenyl)phenol (**6e**) was isolated (40 mg; 14% yield): mp 179 °C (from hexane); UV λ_{max} 241 nm (ϵ 28900); IR (Nujol null) 3200 (br), 3100, 1605, 1550, 1340, 740 cm^{-1}; ^{1}H NMR δ 10.65 (2 H, br), 9.08 (1 H + 1 H, 2 d, J = 2 Hz), 8.88 (1 H + 1 H, 2 d, J = 2 Hz), 7.56–7.25 (7 H + 7 H, m); MS, *m/e* (relative intensity) 286 (M$^+$, 40), 269 (50), 239 (40), 193 (20), 105 (30), 83 (100).

Anal. Calcd for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.49; N, 9.79. Found: C, 59.04; H, 3.54; N, 8.94.

Chromatographic separation afforded 5,7-dinitro-2-phenyl-2,3-dihydrobenzo[*b*]furan **5e** (63 mg; 22% yield): oil; IR (neat) 3100, 1600, 1540, 1350, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.00 (1 H, d, J = 2 Hz), 8.38 (1 H, m), 7.46 (5 H, s), 6.27 (1 H, t, J = 9 Hz), 4.15–3.21 (2 H, m).

5e isomerizes completely to *cis*-2,4-dinitro-(2-phenylethenyl)phenol (**6e**) at room temperature in 48 h. The cis configuration is proposed on the basis of ^{1}H NMR spectrum in comparison to the spectra of *cis*- and *trans*-stilbenes: mp 150–153 °C (from hexane); ^{1}H NMR δ 10.82 (1 H, br), 9.01 (1 H, d, J = 2 Hz), 8.78 (1 H, d, J = 2 Hz), 2.52 (7 H, s); MS, *m/e* (relative intensity) 286 (M$^+$, 100), 269 (95), 239 (100), 199 (45), 180 (55), 165 (87).

Anal. Calcd for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.49; N, 9.79. Found: C, 58.45; H, 3.22; N, 9.53.

Reaction with Vinyl Acetate. Only 5,7-dinitro-2-acetoxy-2,3-dihydrobenzo[*b*]furan (**5f**) was isolated (102 mg; 38%): mp 129–130 °C (needles from chloroform–hexane); UV λ_{max} 283 nm (ϵ 16200), 238 (9700), 204 (9000); IR (Nujol mull) 3100, 1780, 1610, 1380, 1340, 1180, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.01 (1 H, d, J = 2 Hz), 8.51 (1 H, m), 7.28 (1 H, q, J = 4 Hz), 4.06–3.08 (2 H, m), 2.18 (2 H, s); MS, *m/e* (relative intensity) 268 (M$^+$, 7), 208 (100), 180 (7), 149 (21).

Anal. Calcd for $C_{10}H_8N_2O_7$: C, 44.77; H, 2.98; N, 10.45. Found: C, 44.12; H, 2.83; N, 10.20.

Reaction with Isobutyl Vinyl Ether. Only 5,7-dinitro-6-isobutoxy-2,3-dihydrobenzo[*b*]furan (**5g**) was isolated (96 mg; 34% yield): oil; UV λ_{max} 302 nm (ϵ 6400), 250 (10100), 213 (10300); IR (neat) 3080, 1620, 1540, 1350, 1200, 1160, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.03 (1 H, d, J = 2 Hz), 8.46 (1 H, m), 6.25 (1 H, q, J = 4 Hz), 4.01–3.29 (2 H + 2 H, m), 2.03 (1 H, m), 0.96 (6 H, d, J = 8 Hz); MS, *m/e* (relative intensity) 282 (M$^+$, 18), 227 (32), 226 (30), 209 (42), 109 (68), 101 (100), 91 (85).

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[10] Huisgen, R.; Binsch, G.; König, H. *Chem. Ber.* **1964**, *97*, 2884.

Anal. Calcd for $C_{12}H_{14}N_2O_6$: C, 51.06; H, 4.96; N, 9.93. Found: C, 50.25; H, 4.85; N, 9.59.

Photochemical Reactions of 1 with Aromatic Compounds. General Procedure. A suspension of 1 (386 mg, 1 mmol) in acetonitrile (10 mL) and the corresponding aromatic compound (10 mL for benzene, furan, and thiophene and 5 mL for the others) was irradiated under continual stirring until the complete disappearance of 1 (2–4 h). After concentration the solution was either chromatographed on column (silica gel, 2:1 dichloromethan–hexane as eluant) or was extracted with 10% NaOH, and the phenols were obtained after acidification of the alkaline solution.

2,4-Dinitro-6-phenylphenol (7a) (192 mg; 74% yield): mp 202–204 °C (from chloroform–hexane((lit.[11] mp 203–204 °C); MS, *m/e* (relative intensity) 260 (M^+, 100).

2,4-Dinitro-6-(2-furyl)phenol (7b) (175 mg; 70% yield): mp 175–175 °C (from chloroform–hexane); UV λ_{max} 278 nm (ϵ 19000), 240 (11300), 212 (11300); IR (Nujol mul) 3100, 1620, 1590, 1560, 1350, 750 cm^{-1}; ^1H NMR ($CDCl_3$ + Me_2SO-d_6) δ 9.01 (2 H, s), 7.88 (1 H, m), 7.53 (1 H, d, J = 4 Hz), 6.85 (1 H, m), 6.47 (1 H, br); MS, *m/e* (relative intensity) 250 (M^+, 100), 204 (10), 157 (15), 148 (20), 104 (60), 95 (35), 76 (60).

Anal. Calcd for $C_{10}H_6N_2O_6$: C, 48.00; H, 2.40; N, 11.20. Found: C, 48.16; H, 2.24; N, 10.64.

2,4-Dinitro-6-(2-thienyl)phenol (7c) (170 mg; 64% yield): mp 157–159 °C (from chloroform–hexane); UV λ_{max} 397 nm (ϵ 5950), 280 (16100), 242 (13000), 212 (13300); IR (Nujol mull) 3145, 1610, 1560, 1540, 1340, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.55 (1 H, br), 9.01 (1 H, d, J = 2 Hz), 8.78 (1 H, d, J = 2 Hz), 7.78 (1 H, m), 7.53 (1 H, m), 7.30 (1 H, m); MS, *m/e* (relative intensity) 266 (M^+, 100), 250 (13), 220 (21), 173 (15), 145 (26), 111 (35).

Anal. Calcd for $C_{10}H_6N_2O_5S$: C, 45.11; H, 2.25; N, 10.52. Found: C, 45.13; H, 2.21; N, 10.58.

2,4-Dinitro-6-(5-methyl-2-furyl)phenol (7d) (143 mg; 54% yield): mp 165–166 °C (from hexane); UV λ_{max} 283 nm (ϵ 17800), 238 (9000), 210 (9600); IR (Nujol mull) 3145, 3105, 1610, 1560, 1360, 1030, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.93 (2 H, s), 7.71 (1 H, br), 7.20 (1 H, d, J = 4 Hz), 6.25 (1 H, d, J = 4 Hz), 2.45 (3 H, s); MS, *m/e* (relative intensity) 264 (M^+, 100), 218 (8), 109 (15).

Anal. Calcd for $C_{11}H_8N_2O_6$: C, 50.00; H, 3.03; N, 10.60. Found: C, 49.89; H, 2.88; N, 10.20.

From the photoreactions of 1 with anisole and *p*-dimethoxybenzene, 2,4-dinitro-6-phenylphenol (7a) was isolated in 76% and 69% yields, respectively.

Photochemical Reactions of 1 with Alkynes. General Procedure. A suspension of 1 (193 mg, 0, 5 mmol) in acetonitrile (15 mL) and the alkyne (500 mg of diphenylacetylene, diethyl acetylenedicarboxylate, and 2 mL of phenylacetylene) was irradiated for 8 h under continual stirring. After concentration the solution was chromatographed on column (silica gel, 1.5:1 dichloromethane–hexane as eluant). After iodobenzene and excess alkyne, the benzo[*b*]furans **8a–c** were isolated.

5,7-Dinitro-2,3-diphenylbenzo[*b*]furan (8a) (54 mg; 30% yield: mp 221–222 °C (from chloroform–hexane); UV λ_{max} 278 nm (ϵ 3000); IR (Nujol mull) 3100, 1600, 1540, 1340, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.02 (1 H, d, J = 2 Hz), 8.57 (1 H, d, J = 2 Hz), 7.52 (10 H, m); MS, *m/e* (relative intensity) 360 (M^+, 100), 314 (8), 268 (20), 239 (35), 86 (40).

Anal. Calcd for $C_{20}H_{12}N_2O_5$: C, 66.66; H, 3.35; N, 7.77. Found: C, 66.61; H, 3.51; N, 7.56.

5,7-Dinitro-2,3-dicarbethoxybenzo[*b*]furan (8b) (56 mg; 16% yield): mp 115–116 °C (from chloroform–hexane); UV λ_{max} 254 nm (ϵ 30400), 208 (21800); IR (Nujol mull) 3080, 1760, 1740, 1600, 1540, 1350, 1230, 1190, 1150, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 926 (1 H, d, J = 2 Hz), 9.20 (1 H, d, J = 2 Hz), 4.58 (4 H, q, J = 7 Hz), 1.57 (6 H, t, J = 7 Hz); MS, *m/e* (relative intensity) 352 (M^+, 42), 324 (18), 308, 307 (20), 296 (17), 279 (100), 252 (27).

Anal. Calcd for $C_{14}H_{12}N_2O_9$: C, 47.73; H, 3.41; N, 7.95. Found: C, 47.53; H, 3.33; N, 7.71.

5,7-Dinitro-2-phenylbenzo[*b*]furan (8c) (51 mg; 18% yield); mp 136–137 °C (from chloroform–hexane); UV λ_{max} 255 nm (ϵ 2700), 203 (4500); IR (Nujol mull) 3120, 1610, 1540, 1340, 1270, 830 cm^{-1}; ^1H NMR δ 9.01 (1 H, d, J = 2 Hz), 8.76 (1 H, d, J = 2 Hz), 8–7.83 (2 H, m), 7.58–7.43 (3 H, m), 7.25 (1 H, s); MS, *m/e* (relative intensity) 284 (M^+, 100), 238 (38), 192 (44), 180 (22), 163 (42), 139 (29), 102 (54).

Anal. Calcd for $C_{14}H_8N_2O_5$: C, 59.15; H, 2.82; N, 9.86. Found: C, 59.47; H, 2.72; N, 9.43.

Registry No. 1, 89563-18-8; **4a**, 110-83-8; **4b**, 498-66-8; **4c**, 563-79-1; **4d**, 530-48-3; **4e**, 100-42-5; **4f**, 108-05-4; **4g**, 109-53-5; **5a**, 103068-25-3; **5c**, 103068-33-3; **5d**, 103068-26-4; **5e**, 103068-27-5; **5f**, 103068-34-4; **5g**, 103068-35-5; **6a**, 103068-28-6; **6b**, 103068-32-2; **6d**, 103068-29-7; (*E*)-**6e**, 103068-31-1; (*Z*)-**6e**, 103068-30-0; **7a**, 731-92-0; **7b**, 103068-36-6; **7c**, 103068-37-7; **7d**, 103068-38-8; **8a**, 59955-07-6; **8b**, 103068-39-9; **8c**, 17392-13-1; PhH, 71-43-2; $PhOCH_3$, 100-66-3; 4-$H_3COC_6H_4OCH_3$, 150-78-7; furan, 110-00-9; thiophene, 110-02-1; 2-methylfuran, 534-22-5; PhC≡CPh, 501-65-5; $H_3CCH_2O_2CC≡CCO_2CH_2CH_3$, 762-21-0; PhC≡CH, 536-74-3.

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(11) Borsche, W.; Scholten, B. *Chem. Ber.* **1917**, *50*, 596.

9,10-Disubstituted-2-anthracenyl *tert*-Butyl Nitroxides. ESR Spectroscopic Indicators for Singlet Oxygen[1]

John F. W. Keana,* Vaikunth S. Prabhu, Shigeru Ohmiya,[2] and Charles E. Klopfenstein

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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Our purpose is to develop a nitroxide-based ESR probe for singlet oxygen. Among the new anthracenyl nitroxides 1–4 prepared, nitroxide 1 is the most useful. 1 reacts with singlet oxygen to give endoperoxide 18 quantitatively in organic solvents as well as when 1 is incorporated in the bilayers of DMPC vesicles. The reaction is sufficiently rapid and the resulting changes in the ESR spectra are sufficiently characteristic so that the conversion of 1 into 18 may serve as an ESR-based probe for singlet oxygen.

Singlet oxygen[3-5] is an oxidant of broad significance.[6] It is the likely oxidant associated with the photodynamic effect exhibited by biological systems and it may be generated in vivo enzymatically as well.[7] Methods[8] used to

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[1] A portion of this work has been communicated: Keana, J. F. W.; Prabhu, V. S.; Ohmiya, S.; Klopfenstein, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 5020.

[2] On leave from the Deparatment of Medicinal Chemistry, Hoshi College of Pharmacy, Tokyo, Japan.

[3] *Singlet O_2*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1984; Vol. 1–4.

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