g, 5.68×10^{-4} mol) in anhydrous diethyl ether (200 mL) was stirred and cooled in an ice bath. A 2 M diethyl ether solution of a mixture of n-$C_6H_{13}MgBr$ (126.2 g, 0.667 mol) and n-$C_8H_{17}MgBr$ (72.3 g, 0.333 mol) was added and the mixture was allowed to warm to ambient temperature overnight. The contents, which now contained a considerable amount of white solids, were refluxed for another 4 h. The reaction mixture was hydrolyzed by the slow addition to a diluted HCl–ice mixture and phase separated, and the diethyl ether layer was dried and subjected to a rotary vacuum evaporator. The residual pale yellow liquid was dissolved in pentane and passed through an alumina column in order to remove the color. The colorless liquid was subjected to distillation to yield 112.1 g of a liquid: bp 153–84 °C (0.1 mm). A gas chromatographic analysis showed four components with the following GC area percent: **12**, 30%; **13**, 47.8%; **14**, 19.4%; and **15**, 2.8%. The components had the same GC retention time as known standard compounds prepared and fully characterized previously.[2] The mass spectral analysis is shown in Table I.

The other mixtures of trialkylbenzenes shown in Table I were prepared by the same general procedure as described above. The compounds were characterized by comparing the GC retention times with those of known compounds[2] and GC/MS analysis. In experiment 4 (see Table I) only seven of the ten possible components were seen by GC analysis on a 30-m SP2100 capillary column. On mass spectral analysis, three of the GC peaks were found to contain two compounds each (see Table I).

Registry No. 1 (R = n-C_5H_{11}), 111-13-7; **2**, 109-94-4; **7a**, 116785-83-2; **7b**, 14269-14-8; **7c**, 116785-84-3; **8a**, 841-07-6; **8c**, 29536-29-6; **9**, 108-70-3; **10**, 3761-92-0; **11**, 17049-49-9; **12**, 29536-28-5; **13**, 87969-87-7; **14**, 87969-85-5; **15**, 7694-77-1; **16**, 17049-50-2; **17**, 87969-89-9; **18**, 116785-85-4; **19**, 87969-86-6; **20**, 87969-90-2; **21**, 87969-88-8; **22**, 87969-78-6; $NiCl_2$, 7718-54-9; 2-heptanone, 110-43-0; 3-ketooctanal, 3223-40-3.

Photochemical Synthesis of 1-Hydroxyfluorenes: A Correction[1]

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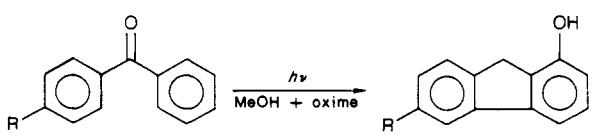
In recent years three publications have appeared,[3] emanating from the same laboratories, in which it is asserted that irradiation of a methanolic solution of benzophenone oxime (quartz) or a mixture of benzophenone and its oxime (Pyrex) gives, in respectiable yield, 1-hydroxyfluorene. The latter was identified by its melting point and that of its acetate[4] and by the mass spectrum, which gave a strong M + 1 peak at m/e 183. An analysis, though referred to,[3c] was not recorded. A variety of data were provided concerning the effect of solvents—the yield in 2-propanol was low and, in acetonitrile, negligible.[3b] Further, the reaction was extended to 4-methyl- and 4-methoxybenzophenone,[3b,c] giving the corresponding, previously unknown 1-hydroxyfluorene derivatives. These



R = H, Me, OMe 1: R = H, Me, OMe

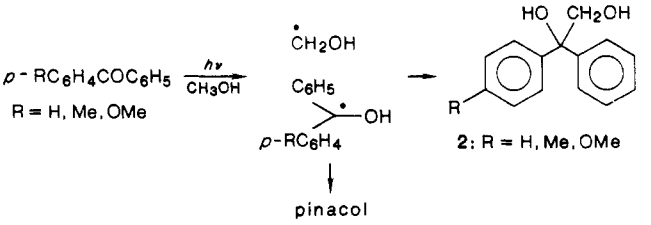
Table I. Melting Points (°C) of 1 and 2

	1[a]	"1"[b]	2[c]	2 (lit.)
R = H	119–120.5 (acetate: 90–91.5)	120 (acetate: 91)	120–121 (benzene)	120–121[d] (monoacetate: 85–86[d])
R = Me		81–82 (74–75)	85 (hexane)	84.5–85.5[e]
R = Me		100–101	105–106 (hexane–benzene)	101–102[f]

[a] Reference 4 [b] Reference 3. [c] This work; recrystallization solvents are given in brackets. [d] Reference 5. [e] Reference 6a. [f] Reference 6b.

were identified by analogy with the unsubstituted derivative and by analysis.[3c] For further information the original papers should be consulted, but it should be noted from the study of mixed ketone–oxime irradiations that the fluorene moiety was derived from the ketone only and that acetone oxime could be substituted for benzophenone oxime.

We were struck by the substantial yield (~65%) from what, if correctly interpreted, must be a lengthy sequence of steps and by the bizarre mechanism indicated. Despite the assertion[3b] that the fluorene was not obtained by irradiation in MeOH in the absence of the oxime, we obtained a substance having the properties described for 1 (R = H), together with benzpinacol and unchanged ketone. The same substance was also obtained when benzophenone and acetone oxime mixture were irradiated in methanol. In the latter experiment, acetone oxime was not consumed (monitored by VPC). Indeed, the reaction of benzophenone in methanol was already described in the literature[5] as giving **2** (R = H). Its melting point and that of its acetate are those recorded[5] for **2** (R = H) (Table I) (and, *by coincidence are also those of 1 (R = H) and its acetate*). The formation of **2** is unexceptional, being a consequence of H abstraction from the solvent followed by cage combination of the resultant ketyl and hydroxymethyl radicals. The diol **2** (R = H) gave a very strong M – 31 peak (at m/e 183) in the 70 eV mass spectrum: the parent ion was only detected at 30 eV.



In a similar way irradiation of 4-methylbenzophenone and 4-methoxybenzophenone gave **2** (R = Me) and **2** (R = OMe) with the melting points and other properties ascribed[3b] to **1** (R = Me) and **1** (R = OMe). These derivatives of **2** are known substances[6] (see Table I). We conclude, therefore, that despite minor anomalies remaining (see Experimental Section) the claim of photochemical formation of 1-hydroxyfluorene is in error.

Experimental Section

Chemicals. Acetone oxime was crystallized from hexane; the benzophenones were available in the laboratory; 80-200 mesh silica

(1) Publication No. 401 from the Photochemistry Unit, University of Western Ontario.
(2) Holder of NSERC Summer Scholarship.
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gel (Mallinckrodt) and neutral alumina (Fisher) were used for column chromatography.

General Irradiation Procedure. Irradiations were carried out under an argon atmosphere in an immersion well apparatus (water cooled) with a Hanovia 450-W medium pressure mercury lamp (Pyrex filter). Methanol solutions (350 mL) of benzophenones (15–17.5 mmol) and acetone oxime (1.17 g) were irradiated for 4 h.[7] After the irradiation the solvent methanol was removed under reduced pressure and the residue was chromatographed over neutral alumina or silica gel[8] and eluted with hexane–ether (0–100%) mixtures and finally with methylene chloride. The pinacols[9] were eluted first in hexane–ether (<50%) followed by the diols **2** in more polar eluant mixtures. The melting points of the recrystalized products (capillary) are uncorrected. Yields represent the isolated amounts after chromatography.

1,1-Diphenyl-1,2-ethanediol (2, R = H): yield 44%, mp 120–121 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.80 (1 H, br, OH), 3.20 (1 H, br, OH), 4.17 (2 H, s, CH_2), and 7.20–7.46 ppm (10 H, m, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) 69.33 (t, CH_2OH), 78.54 (s, COH), 126.39 (d), 127.42 (d), 128.39 (d), and 143.81 ppm (s); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 183 (100), 105 (87.5), and 77 (39); (30 eV) M^+ ion detected at *m/e* 214 (0.2).

1-Phenyl-1-*p*-tolyl-1,2-ethanediol (2, R = Me): yield 40%, mp 85 °C; ^{1}H NMR (CCl_4, 200 MHz) 2.28 (3 H, s, CH_3), 2.60 (1 H, br, OH), 3.46 (1 H, br, OH), 3.78 (2 H, br,[10] CH_2), 6.95–7.26 ppm (9 H, m, Ar); ^{13}C NMR (acedone-d_6, 75.4 MHz) 20.93 (q), 69.53 (t, CH_2OH), 78.63 (s, COH), 127.23 (d), 127.29 (d), 127.32 (d), 128.47 (d), 129.16 (d), 136.64 (s), 143.56 (s), and 146.66 ppm (s); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 197 (100), 119 (26.5), 105 (49.5), 91 (9.5), and 77 (7.5); (30 eV) M^+ ion detected at *m/e* 228 (0.4).

1-Phenyl-1-(*p*-methoxyphenyl)-1,2-ethanediol (2, R = OMe): yield 32%, mp 105–106 °C; ^{1}H NMR (CCl_4, 200 MHz) 1.66 (1 H, br, OH), 2.92 (1 H, br, OH), 3.75 (3 H, s, OMe), 3.95 (2 H, slightly br,[10] CH_2), and 6.70–7.36 ppm (9 H, m, Ar); ^{13}C NMR (acedone-d_6, 75.4 MHz) 55.35 (q), 69.23 (t, CH_2OH), 78.49 (s, COH), 113.84 (d), 127.22 (d), 127.34 (d), 128.47 (d), 128.58 (d), 138.57 (s), 146.80 (s), and 159.27 ppm (s); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 244 (3.2) M^+ ion, 227 (2.8), 213 (100), 135 (67.5), 105 (92), and 77 (28.5).

(7) VPC analysis (10% OV-101 on HP Chromosorb W at 40 °C) of aliquots withdrawn before and after irradiation indicated no loss of acetone oxime. A similar irradiation of benzophenone in the absence of acetone oxime gave pinacol and the diol **2** (R = H) in identical yields. The reaction was nearly complete after this period and only small amounts (<2%) of ketone were left unreacted.

(8) The photolysis products from 4-methyl- and 4-methoxybenzophenones showed some decomposition on an alumina column and hence were chromatographed on silica gel.

(9) Along with the pinacol(s), unchanged ketone and acetone oxime were also eluted: they were removed by washing the solid pinacol(s) with hexane. 4-Methyl- and 4-Methoxybenzophenones gave mixture of pinacols (*dl* and *meso*) in nearly a 1:1 ratio.

(10) This CH_2 signal appears as sharp singlet in $CDCl_3$ solvent and the observed broadening may be associated with enantiotopic properties of the methylene protons.

Synthesis of 4,6-Dinitroresorcinol

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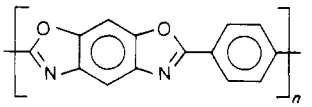
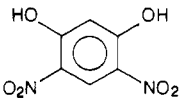
Polyhydroxy aromatics are typically difficult to nitrate directly in large quantities because of the exothermicity of the nitration reaction.[1] Also, the desired regiospecificity may be difficult to obtain in the nitration of phenols because of their reactivity. However, recent developments in the synthesis of the high strength, liquid crystalline polymer poly[*p*-phenylenebenzobis(oxazole)] (PBO)[2] require a high-yield, regioselective synthesis of 4,6-dinitroresorcinol (4,6-DNR)[2] as a polymer precursor.

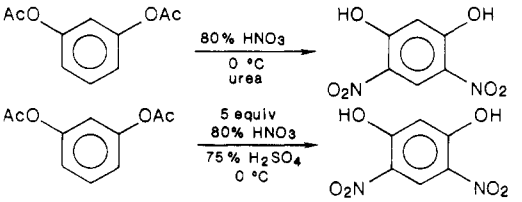


PBO



DNR

Most of the relevant organic literature pertains to the synthesis of 2,4-dinitroresorcinol.[3-6] Only a few references are available for the direct synthesis of 4,6-DNR, and only very low yields were obtained.[7] It is recognized that the 2,4-substitution evolves from prior nitrosation,[8] and thus we have focused on nitration with strict control of nitrosation reactions. Consequently, we have found that 4,6-DNR can be synthesized in high yield from resorcinol diacetate with nitric acid or mixed solutions of nitric acid/sulfuric acid containing large quantities of urea as a nitrous acid trap. Typical optimal yields for the two



systems are 44 and 60%, but the yields are quite sensitive to conditions. Our experiments demonstrated that if the nitric acid concentration or the sulfuric acid concentration is varied by 5% in either direction or if the temperature rises above +10 °C, an extremely low yield of 4,6-DNR is obtained.

In conclusion, we developed a convenient method for synthesizing 4-substituted resorcinols. This reaction requires the control of all prior nitrosation reactions to minimize the side reactions and to maximize both the regioselectivity of the reaction and the yield.

Experimental Section

Preparation of Purified Nitric Acid. Nitrous acid reacts with resorcinol or an acylated resorcinol to give 2-nitrosoresorcinol. Thus, control of nitrous acid is essential to obtain 4,6-DNR. The 90 wt % white fuming nitric acid and the 70 wt % nitric acid were prepared by bubbling dry oxygen or air through 90 wt % red nitric acid to remove the NO_2 or N_2O_4 until the nitric acid was colorless. Residual nitrous acid was then eliminated from either nitric acid concentration by addition of urea or hydrazine. Urea was added in excess to destroy any nitrous acid that might remain or that was formed during the nitration reaction.

Synthesis in Nitric Acid. *CAUTION*: This synthesis has inherent dangers. This reaction involves solutions of nitric acid and resorcinol diacetate, which have been known to react violently after an induction period (fume off)!! 2,4,6-Trinitroresorcinol (styphnic acid—*CAUTION*—explosive!!) is formed as a byproduct in this reaction.

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