NMR δ 9.50 (d, 1 H, CHO, J = 1.6 Hz), 7.35 (m, 10 H, ArH), 7.17m (d, 1 H, J = 8.4 Hz, ArH), 6.90 (d, 1 H, J = 8.4 Hz, ArH), 5.28 (s, 2 H, CO_2CH_2Ph), 4.89 (s, 2 H, $ArOCH_2Ph$), 2.54 (m, 2 H, $ArCH_2$), 2.29 (s, 3 H, $ArCH_3$), 2.20 (m, 1 H, $CHCHO$), 1.93 (m, 1 H), 1.55 (m, 1 H), 1.03 (d, 3 H, J = 6.5 Hz, $CHCH_3$); IR 1726, 1455, 1277, 1255, 1134 cm^{-1}; $[\alpha]^{25}_D$ = +8.3° (c 0.0145 CCl_4); HRMS (m/e) found 416.1986, calculated for $C_{27}H_{28}O_4$ 416.1987.

Supplementary Material Available: ^1H NMR spectra of compounds **2**, **3**, **6–8**, and **9a–c** (10 pages). Ordering information is given on any current masthead page.

A New Preparation of Ethyl 3-Oxo-4-pentenoate: A Useful Annelating Reagent

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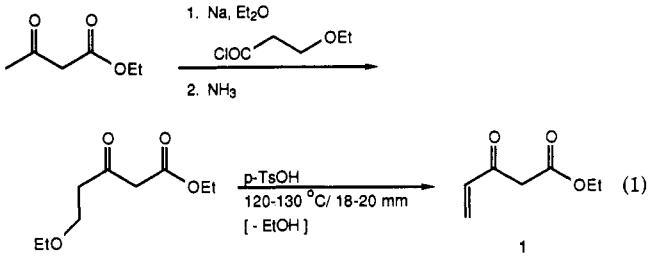
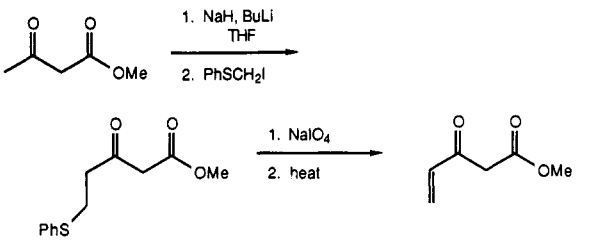
As part of a continuing project directed toward the total synthesis of several terpenes, we required large amounts of the well-known annelating reagent ethyl 3-oxo-4-pentenoate (**1**, Nazarov's reagent).[1] The synthesis and use of this compound as an annelating agent have been reported in the literature many times.[2-9] We required a facile, short, and efficient synthesis of **1**, readily providing large quantities.

In 1953, Nazarov reported the preparation of ethyl 3-oxo-4-pentenoate (**1**) as shown in eq 1. The last step of



(1)

this synthesis required the elimination of ethanol through acid catalysis. Groups prior to us have termed this step "capricious",[10] and indeed, we were unable to obtain more than 100 mg of **1** by this method. Furthermore, attempted elimination of HCl from ethyl 5-chloro-3-oxo-pentanoate[11] in an analogous manner also failed.[12] The synthesis of methyl 3-oxo-4-pentenoate by Stork and Guthikonda[4] (64–68% for three steps) required as the last step a retro-Diels–Alder reaction of pentadiene through a special high-temperature apparatus (quartz-packed column at 600 °C). Trost and Kunz[6] later reported preparation of the methyl ester of **1** wherein the last step involved elimination of a sulfoxide as shown in eq 2 (60–76% for three steps). Also, (iodomethyl)phenylsulfide utilized here must be prepared from thioanisole requiring two steps (89%). In our hands, the elimination occurred smoothly, but polymerization proceeded promptly.

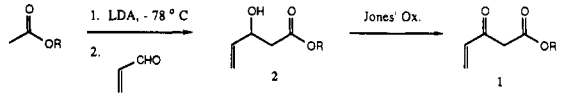


(2)

We wish to report a facile (two step) and efficient synthesis of several esters of 3-oxo-4-pentenoate. It is well-known that the one-step preparation of β-keto esters is a difficult task since acylation of an ester enolate generates a product that contains protons more acidic than the starting materials, often resulting in bisacylation.[13] Indeed, our attempts to acylate lithioethyl acetate using acryloyl chloride failed to provide more than minute quantities of ethyl 3-oxo-4-pentenoate.

As shown in a study by Smith and Levenberg,[14] β-keto esters can be synthesized readily by oxidation of the corresponding β-hydroxy esters. We therefore prepared a series of β-hydroxy esters (**2a–e**, Table I) to explore oxidation to Nazarov's reagent and analogues. Typically, the ester enolate (100 mmol, LDA, THF, –78 °C) was reacted with acrolein to provide in all cases good yields of β-hy-

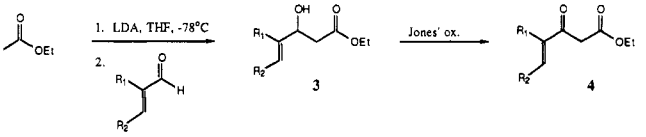
Table I



entry	R	solvt	% yield of **2** (scale)	% yield of **1** (scale)
1	**a**, Me	THF	71 (100 mmol)	48 (50 mmol)
2	**b**, Et	THF	79 (100 mmol)	58 (50 mmol)
3	**b**, Et	Et_2O	*a* (300 mmol)	53[b]
4	**c**, *i*-Pr	THF	76 (100 mmol)	76 (50 mmol)
5	**d**, *t*-Bu	THF	74 (100 mmol)	64 (50 mmol)
6	**e**, bornyl	Et_2O	95 (100 mmol)	59 (50 mmol)

[a] Compound **2b** was not purified in this case, rather the oxidation carried out on crude material. [b] The percent yield in this case is for two steps.

Table II



entry	compd	% yield of **3** (scale)	% yield of **4** (scale)
1	**a**, R_1 = CH_3, R_2 = H	89 (100 mmol)	42 (50 mmol)
2	**b**, R_1 = H, R_2 = CH_3	89 (100 mmol)	54 (50 mmol)

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(2) Pelletier, S. W.; Chappell, R. L.; Prabhakar, S. *J. Am. Chem. Soc.* **1968**, *90*, 2889. Stork, G.; Guthikonda, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 5109.
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(10) Ellis, J. E.; Dutcher, J. S.; Heathcock, C. H. *Synth. Commun.* **1974**, *4*, 71.
(11) Prepared by the reaction of lithioethyl acetate with 3-chloropropionyl chloride.
(12) This has been done successfully to prepare *tert*-butyl 3-oxo-4-pentenoate, see: Ohta, S.; Shimabayashi, A.; Hatano, S.; Okamoto, M. *Synthesis* **1983**, 715.
(13) Pollet, P.; Gelin, S. *Synthesis* **1978**, 142.
(14) Smith III, A. B.; Levenberg, P. A. *Synthesis* **1981**, 567.

0022-3263/89/1954-4717$01.50/0

droxy esters.[14] Oxidation occurred smoothly using Jones' reagent[15] to provide the volatile β-keto esters (**1a–e**) in all cases. Furthermore, methacrolein and crotonaldehyde were also suitable reactants, providing ample quantities of the annelating agents **4a–b**[4,13] (Table II). All products were isolated by Kugelrohr distillation with the receiving bulb cooled to −78 °C, thereby eliminating the need for chromatography. Furthermore, the annelating agents could be stored at −20 °C for several months without decomposition.[4]

Our new preparation of ethyl 3-oxo-4-pentenoate and analogous esters proceeds in 34–58% yield[16] for two steps from readily available starting materials and is amenable to scale-up without consequence.[17] Reports on the applications of these annelating agents will be forthcoming.

Experimental Section

General Procedure. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 125 MHz, respectively, on a General Electric QE-300 spectrometer. Infrared spectra were recorded on an IBM FTIR 32 spectrometer. Mass spectra were obtained on a Finnegan Model 4500 GC/MS/DS using CI. The elemental analyses were performed by E&R Microanalytical Laboratories, Corona, NY. THF was distilled from sodium/benzophenone ketyl prior to use. Anhydrous ether was obtained from Fisher with a fresh 1-L container used for each reaction. Diisopropylamine was distilled from NaOH. The esters were dried and distilled prior to use. Acrolein was obtained from Aldrich and distilled immediately prior to use (25 mmHg). All other reagents were obtained commercially and used as purchased.

Esters of 3-Hydroxy-4-pentenoate. To a stirred solution of THF (400 mL) and diisopropylamine (15.4 mL, 110 mmol) at −78 °C was added *n*-BuLi (44 mL, 110 mmol, 2.5 M in hexanes). The reaction was stirred at −78 °C for 15 min followed by the dropwise addition to ester (100 mmol) at a rate such that the *internal* reaction temperature remained below −68 °C. Upon completion of addition of ester, the reaction was stirred for 50 min. Distilled acrolein (6.7 mL, 100 mmol) in 50 mL of THF was added via cannula, and the reaction stirred at −78 °C for 5 min. The reaction was quenched by the rapid injection of a saturated NH_4Cl solution (30 mL), immediately poured into a separatory funnel containing diethyl ether (200 mL), and washed with brine (2 × 100 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated in vacuo to give a yellow oil which was purified by Kugelrohr distillation with the receiver bulb cooled to −78 °C.

Methyl 3-hydroxy-4-pentenoate (2a): bp 58 °C/0.50 mmHg (Kugelrohr oven temperature); R_f (hexanes:ethyl acetate 3:1) 0.21; IR (film) 3426, 2982, 1730, 1375, 1275, 1180, 1109 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.45–2.62 [m, 2 H, HC(OH)CH_2C(O)], 2.91 (d, 1 H, 4.3 Hz, O*H*), 3.71 (s, 3 H, OCH_3), 4.5–4.6 [br m, 1 H, *H*C(OH)C], 5.1–5.8 (m, 2 H), 5.8–5.9 (m, 1 H); MS, *m/z* 131 (MH^+). Anal. Calcd for $C_6H_{10}O_3$: C, 55.38; H, 7.76. Found: C, 55.20; H, 7.95.

Ethyl 3-hydroxy-4-pentenoate (2b): bp 57 °C/0.60 mmHg (oven temperature; lit.[14] bp 42 °C/0.125 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.26; IR (film) 3437, 2984, 2938, 1732, 1373, 1275, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3 H, *J* = 6.7 Hz, OCH_2CH_3), 2.4–2.6 [m, 2 H, C(OH)CH_2C(O)], 3.15–3.25 (br m, 1 H, O*H*), 4.10 (q, 2 H, *J* = 6.7 Hz, OCH_2CH$_3$), 4.44–4.57 [m, 1 H, *H*C(OH)], 5.05–5.35 (m, 2 H), 5.78–5.90 (m, 1 H); MS, *m/z* 145 (MH^+).

Isopropyl 3-hydroxy-4-pentenoate (2c): bp 70 °C/0.52 mmHg (oven temperature); R_f (hexanes:ethyl acetate 3:1) 0.30; IR (film (3441, 2984, 1728, 1375, 1275, 1179, 1109, 928 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 6 H, *J* = 6.2 Hz, [OCH(CH_3)$_2$], 2.4–2.58 [m, 2 H, CH(OH)CH_2C(O)], 3.20 (d, 1 H, 4.4 Hz), 4.42–4.52 (br m, 1 H, O*H*), 4.9–5.1 [m, 1 H, OC*H*(CH$_3$)$_2$], 5.11–5.3 (m, 2 H, H_2C=CH), 5.8–5.9 (m, 1 H, H_2C=C*H*); MS, *m/z* = 159 (MH^+). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.94. Found: C, 60.49; H, 9.20.

***tert*-Butyl 3-hydroxy-4-pentenoate (2d)**: bp 58 °C/1.54 mmHg (oven temperature); R_f (hexanes:ethyl acetate 3:1) 0.34; IR (film) 3420, 2980, 2934, 1721, 1368, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 [s, 9 H, OC(CH_3)$_3$], 2.35–2.51 [m, 2 H, HC(OHCH_2C(O)], 3.17–3.25 (br s, 1 H, O*H*) 4.42–4.53 [br m, 1 H, *H*C(OH)], 5.1–5.3 (m, 2 H), 5.87 (m, 1 H); MS, *m/z* 173 (MH^+). Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.38. Found: C, 62.51; H, 9.64.

Bornyl 3-hydroxy-4-pentenoate (2e): Compound **2e** was prepared from (−)-bornyl acetate and acrolein as described above; however, anhydrous ether was used as solvent. Purification of bornyl 3-hydroxy-4-pentenoate was achieved by Kugelrohr distillation utilizing a preheated oven (110 °C) at 0.40 mmHg; R_f (hexanes:ethyl acetate 3:1) 0.37; IR (film) 3440, 2955, 2882, 1734, 1306, 1271, 1181, 1115, 1020, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 3 H), 0.90 (s, 3 H), 0.95 (s, 3 H), 1.2–1.4 (m, 2 H), 1.85–1.95 (m, 3 H), 2.3–2.4 (m, 1 H), 2.45–2.65 (m, 2 H), 3.1–3.2 (m, 1 H), 4.5–4.6 (br m, 1 H), 4.9–5.0 (br m, 1 H), 5.1–5.38 (m, 2 H), 5.8–5.95 (m, 1 H). Anal. Calcd for $C_{15}H_{23}O_3$: C, 71.67; H, 9.24. Found: C, 71.84; H, 9.11.

The condensations of methacrolein and crotonaldehyde with ethyl acetate were carried out in an analogous manner.

Ethyl 3-hydroxy-4-methyl-4-pentenoate (3a): bp 74 °C/0.37 mmHg (oven temperature); R_f (hexanes:ethyl acetate 3:1) 0.32; IR (film) 3449, 2982, 1732, 1447, 1372, 1275, 1163, 1024, 903 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3 H, *J* = 7.2 Hz), 1.70 (s, 3 H), 2.44–2.58 (m, 2 H), 3.15–3.21 (br s, 1 H), 4.10 (q, 2 H, *J* = 7.2 Hz), 4.41 (app t, 1 H), 4.81 (s, 1 H), 4.97 (s, 1 H). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.94. Found: C, 60.99; H, 9.14.

Ethyl 3-hydroxy-5-methyl-4-pentenoate (3b): bp 56 °C/0.4 mmHg (oven temperature; lit.[18] bp 68 °C/0.5 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.28; IR (film) 3443, 2982, 1734, 1374, 1248, 1028, 966 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3 H, *J* = 7.2 Hz), 1.62 (d, 3 H, *J* = 6 Hz), 2.46 (d, 2 H, *J* = 6.4 Hz), 3.03 (d, 1 H, *J* = 4.2 Hz), 4.10 (q, 2 H, *J* = 7.2 Hz), 4.4–4.5 (br m, 1 H), 5.4–5.5 (m, 1 H), 5.6–5.75 (m, 1 H). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.94. Found: C, 60.98; H, 9.14.

Esters of 3-Oxo-4-pentenoate. Jones' reagent was prepared by the addition of concentrated H_2SO_4 (30 mL) to CrO_3 (33.5 g) followed by the careful dilution with water (to give 250 mL of total solution).[15] Then, Jones' reagent (51 mL, 51 mmol) was added dropwise to a stirred solution of β-hydroxy ester (50 mmol) in acetone (200 mL) at 0 °C. After complete addition of the oxidizing agent, the mixture was allowed to reach room temperature and stirred until the reaction reached completion as determined by the absence of starting material by thin-layer chromatography (3–24 h). Methanol (20 mL) was added to quench excess Jones' reagent. The reaction mixture was poured into a separatory funnel and extracted with diethyl ether (200 mL). The organic extracts were washed with water (3 × 100 mL) and then brine (100 mL). The organic layer was dried ($MgSO_4$) and filtered, and the solvent removed by *simple distillation* which gave a light yellow oil. Purification was achieved by Kugelrohr distillation with the receiver bulb cooled to −78 °C.

Methyl 3-oxo-4-pentenoate (1a): bp 23 °C/0.40 mmHg (oven temperature; lit.[4,6] bp 78–81 °C/18 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.49; IR (film) 2957, 1745, 1660, 1402, 1240, 1151, 1043, 1028, 814 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.59 [s, ketonic H at C(2)], 3.68 (m, 3 H), 5.03 [s, enolic H at C(2)], 5.49 (app t, 1 H), 5.90–6.40 (m, 2 H), 11.7 (s, enol O*H*); MS, *m/z* 129 (MH^+).

Ethyl 3-oxo-4-pentenoate (1b): bp 45 °C/0.60 mmHg (oven temperature; lit.[1,5] bp 76–78 °C/18 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.53; IR (film) 2984, 1741, 1659, 1588, 1423, 1242, 1150, 1038, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (overlapping t, 3 H), 3.6 [s, ketonic H at C(2)], 4.1–4.3 (m, 2 H), 5.05 [s, enolic H at C(2)], 5.50 (app t, 1 H), 5.91–6.43 (m, 2 H), 11.8 (s, enol O*H*); MS, *m/z* 143 (MH^+).

Isopropyl 3-oxo-4-pentenoate (1c): bp 63 °C/0.60 mmHg (oven temperature); R_f (hexanes:ethyl acetate 3:1) 0.57; IR (film) 2984, 2940, 1738, 1659, 1590, 1421, 1375, 1356, 1239, 1150, 1107,

(15) For preparation of the Jones' reagent, see: Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39. Other oxidizing agents such as pyridinium chlorochromate, pyridinium dichromate, and Swern (DMSO, oxalyl chloride) were explored; however, the Jones' method gave superior results in all cases. Use of the Jones' reagent is operationally simple and relatively inexpensive.

(16) The overall yield of methyl 3-oxo-4-pentenoate (**1a**) is low due to the extreme volatility of this compound.

(17) To date, we have successfully carried out this reaction on a 300-mmol scale. See Table I, entry 3.

(18) Nakamura, E.; Shimizu, M.; Kuwajima, I. *Tetrahedron Lett.* **1976**, *17*, 1699.

814 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (overlapping d, 6 H), 3.6 [s, ketonic H at C(2)], 5.05 [s, enolic H at C(2)], 5.1–5.2 (m, 1 H), 5.53 (app t, 1 H), 5.93–6.46 (m, 2 H), 11.9 (s, enol O*H*); MS, *m/z* 157 (MH^+). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.76. Found: C, 61.76; H, 7.93.

***tert*-Butyl 3-oxo-4-pentenoate (1d)**: bp 49 °C/0.72 mmHg (oven temperature; lit.[12] bp 80–82 °C/5 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.61; IR (film) 2982, 2934, 1736, 1658, 1587, 1418, 1370, 1254, 1146, 814 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (m, 9 H), 3.51 [(s, ketonic H at C(2)], 4.96 [s, enolic H at C(2)], 5.47 (t, J = 6 Hz, 1 H), 5.9–6.4 (m, 2 H), 11.9 (s, enol O*H*); MS, *m/z* 171 (MH^+).

Bornyl 3-oxo-4-pentenoate (1e): Compound **1e** was prepared as described above; however, ether was used as the reaction solvent. Purification was achieved by Kugelrohr distillation utilizing a preheated oven (150 °C) at 0.51 mmHg. R_f (hexanes:ethyl acetate 3:1) 0.59; IR (film) 2953, 1740, 1657, 1588, 1420, 1244, 1150, 1040, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.0 (m, 9 H), 1.0–1.1 (m, 1 H), 1.2–1.4 (m, 2 H), 1.6–2.0 (m, 3 H), 2.3–2.45 (m, 1 H), 3.7 [s, ketonic H at C(2)], 4.9–5.0 (m, 1 H), 5.15 [s, enolic H at C(2)], 5.35 (app t, 1 H), 6.0–6.5 (m, 2 H), 11.85 (s, enol O*H*). Anal. Calcd for $C_{15}H_{21}O_3$: C, 72.25; H, 8.51. Found: C, 72.28; H, 8.58.

Compounds 4a and **4b** were prepared in an analogous fashion.

Ethyl 4-methyl-3-oxo-4-pentenoate (4a): bp 48 °C/0.37 mmHg (oven temperature; lit.[4,19] bp 88–92 °C/12 mmHg); R_f (hexanes:ethyl acetate 3:1) 0.61; IR (film) 2984, 1741, 1672, 1636, 1601, 1421, 1239, 1152, 1040, 968 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–1.4 (m, 3 H), 1.82–1.95 (m, 3 H), 3.54 [s, ketonic H at C(2)], 4.15–4.23 (m, 2 H), 4.93 [s, enolic H at C(2)], 5.75–6.2 (m, 1 H), 6.6–7.0 (7, 1 H), 11.86 (s, enol O*H*). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.76. Found: C, 61.69; H, 7.95.

Ethyl 5-methyl-3-oxo-4-pentenoate (4b): bp 78 °C/1.60 mmHg (oven temperature; lit.[4,19,20] bp 95–98 °C/mmHg); R_f (hexanes:ethyl acetate 3:1) 0.49; IR (film): 3101, 2986, 1743, 1682, 1595, 1456, 1420, 1379, 1345, 1294, 1250, 1095, 1034, 941 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–1.35 (m, 3 H), 1.86 (s, 3 H), 3.70 [s, ketonic H at C(2)], 4.15–4.25 (m, 2 H), 5.18 [s, enolic H at C(2)], 5.3–5.9 (m, 2 H), 12.0 (s, enol O*H*). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.76. Found: C, 61.55; H, 7.78.

Acknowledgment. R.Z. acknowledges the Camille and Henry Dreyfus Foundation for a Distinguished New Faculty Grant and the American Cancer Society, Inc., for a Junior Faculty Grant. This work was supported by the Biomedical Research Support Grant Program (S07 RR07068-23), Division of Research Resources, National Institutes of Health and Syracuse University.

Supplementary Material Available: ^{13}C NMR data (recorded at 125 MHz) for all products (2 pages). Ordering information is given on any current masthead page.

(19) Couffignal, R.; Moreau, J.-L. *J. Organomet. Chem.* **1977**, *127*, C65.
(20) Bodalski, R.; Pietrusiewicz, K. M.; Monkiewicz, J.; Koszuk, J. *Tetrahedron Lett.* **1980**, *21*, 2287.

Oxidation of 4-(Phenylazo)-1,2-naphthalenediol

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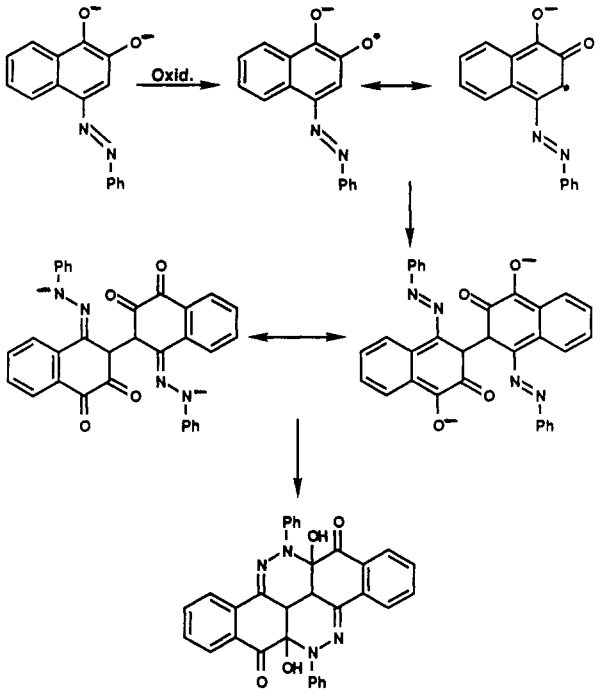
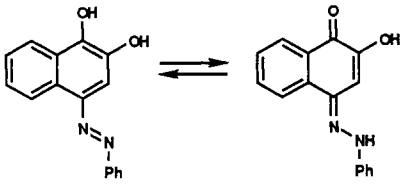
Received March 17, 1989

An alkaline solution of 4-(phenylazo)-1,2-naphthalenediol (1) can develop silver in an exposed photographic emulsion and produce a lemon-yellow image.[2]

Scheme I. Possible Mechanism for the Formation of 2



Under appropriate conditions, after neutralization, an apparently colorless image against an orange background of the unreacted dye can be obtained.[3] The oxidation of 1 in aqueous alkali has been reported twice, originally by Zincke and Wiegand in 1895,[4] and again by Shemyakina, Bogoslovsky, and Shemyakin.[5] The deep blue alkaline solution of the dye turns brown on exposure to air and deposits a yellow solid which was described in each case as 4-(phenylazo)-1,2-naphthoquinone.



1a **1b**

To understand the photographic experiments we have oxidized 1 with silver nitrate in potassium hydroxide solution. Workup of the alkaline mixture without neutralization yielded the yellow product in 37% yield after recrystallization.[6] The yellow product was shown by IR and ^{1}H NMR spectroscopy and by TLC to be identical with the product of air oxidation, and also (by TLC and MS only) with a yellow product obtained by extraction of some of the apparently colorless image material mentioned above.

The mass spectrum of the yellow product showed it to be a dehydro dimer with a molecular ion at *m/e* 526 (EI) and little evidence of fragmentation except for a small peak at *m/e* 490. The IR spectrum (CCl_4) contained a strong carbonyl band at 1698 cm^{-1} and an NH or OH band at 3480 cm^{-1}. The proton NMR spectrum showed a nonex-

(1) Present address: Anitec Image Corp., 40 Charles St., P.O. Box 4444, Binghamton, NY 13902-4444.
(2) Friedman, J. S. *History of Color Photography*; Focal: New York, 1968; p 367.
(3) Rogers, H. G., Personal communication.
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(6) The same result is obtained using $K_3Fe(CN)_6$ in aqueous KOH.

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