nochloridate **3** and starting phosphinothiolate **1** involves a second inversion at the phosphoryl center which consequentially results in retention of configuration. Racemization, instead, arises from the decomposition of the salt **7**, which leads to one molecule with unchanged configuration and another that is inverted.

It is interesting to note that in the case of the reaction involving nearly complete retention of configuration, namely, chlorination with sulfuryl chloride in toluene, only traces of the salt **7** are observed. In contrast, when the chlorinating agent was elemental chlorine in methylene chloride, the amount of the salt **7** observed was considerably greater, and at the same time appreciable racemization took place. Specific rotations and optical yields for chlorination reactions performed at 0 °C are included in Table I.

Participation of transient species containing two phosphorus atoms was also demonstrated in other types of organic phosphorus thioloesters and will be a topic of future publications.

This communication resolves the problem of the reaction mechanism of halogenolysis of the phosphorus–sulfur bond in 4-coordinated organophosphorus compounds via the combined results of the stereochemical investigations and the structural studies accomplished by ^{31}P NMR spectroscopy of the reaction intermediates. Another important aspect of this paper is the demonstrated facile formation of the P–O–P system by nucleophilic attack of phosphoryl oxygen on the 4-coordinated phosphorus center. This result confirms the reaction schemes proposed earlier for a number of reactions, important from the synthetic point of view of the organophosphorus compounds[10] and polymers.[11]

Acknowledgment. This work was supported by the Polish Academy of Sciences (Project MR.I.12).

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(10) (a) Kosolapoff, G. M.; Watson, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 4101, 5466. (b) Kosolapoff, G. M. *Science (Washington, D.C.)* **1948**, *108*, 485. (c) Toy, A. D. F. *J. Am. Chem. Soc.* **1949**, *71*, 2268. (d) Aaberg, T.; Gramstad, T.; Husebye, S. *Tetrahedron Lett.* **1979**, 2263.

(11) Vogt, W. *Macromol. Chem.* **1973**, *163*, 89.

(12) Luckenbach, R. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1977**, *32B*, 584.

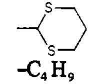
B. Krawiecka, J. Michalski,* E. Tadeusiak
Centre of Molecular and Macromolecular Studies
Polish Academy of Sciences
90-362 Łódź, Boczna 5, Poland

Received March 25, 1980

Arene–Metal Complexes in Organic Synthesis: Addition to Styrene-Type Ligands

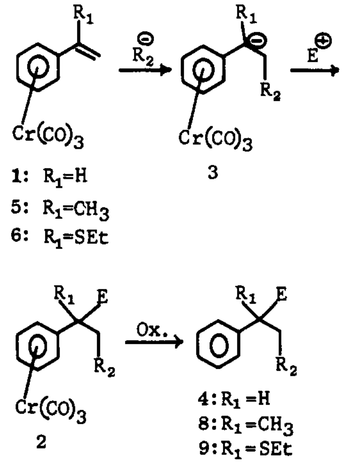
Sir:

Table I. Addition of Carbon Anions to Styrene–Cr(CO)$_3$ Derivatives

entry	complex	anion unit, R_2	electrophile	product(s), yield,[a] %
1	1	–C(CH$_3$)$_2$CN	H$^+$	4: E = H, 92
2	1	–C(CH$_3$)$_2$CN	CH$_3$I	4: E = CH$_3$, 82
3	1	–C(CH$_3$)$_2$CN	CH$_3$COCl	4: E = COCH$_3$, 71
4	1	–(CH$_3$)$_2$CO$_2$-*t*-Bu	H$^+$	4: E = H, 73
5	1	–C(CN)(OR)CH$_3$[c]	H$^+$	4: E = H, 75[b]
6	5	–C(CH$_3$)$_2$CN	H$^+$	8: E = H, 34
7	5	–C(CN)(OR)CH$_3$[c]	H$^+$	8: E = H, 62[b]
8	6	–C(CH$_3$)$_2$CN	H$^+$	9: E = H, 62
9	6	–C(CH$_3$)$_2$CN	PhSSPh	9: E = SPh, 59[d]
10	6	–C(CN)(OR)CH$_3$	H$^+$	9: E = H, 81[b,e]
11	6		H$^+$	9: E = H, 41
12	6	–C$_4$H$_9$	H$^+$	9: E = H, 61
13	6	–Ph	H$^+$	9: E = H, 84
14	6	–CH$_3$	H$^+$	9: E = H, 60
15	7	–C(CH$_3$)$_2$CN	H$^+$	12, 100
16	7	–C(CH$_3$)$_2$CN	CH$_3$I	14, 75
17	7	–C(CH$_3$)$_2$CN	PhCOCl	15, 32

[a] The yield refers to isolated product after oxidation of the inter-intermediate complexes. [b] The product has R_2 = COCH$_3$, obtained after hydrolysis of the cyanohydrin acetal; see: G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, 93, 5286 (1971). [c] R = CH(CH$_3$)OCH$_2$CH$_3$. [d] Characterized as the hydrolysis product of the bisthioketal. [e] The product is 4-phenyl-3-buten-2-one obtained after hydrolysis of the cyanohydrin acetal and base-promoted elimination of the ethylthio group.

The special reactivity of arene rings coordinated to transition metals has been developed into useful synthesis methodology.[1] An important effect is the electron-accepting power of the chromium tricarbonyl unit, which promotes nucleophilic addition to the arene ring in arene–Cr(CO)$_3$ complexes[2] and strongly increases the kinetic acidity of benzylic hydrogens.[3] Complexes of η^6-styrene with Cr(CO)$_3$ have been known for many years,[4] and it was recognized early that nucleophilic addition to the β position of an η^6-styrene ligand would generate the stabilized benzyl anion (e.g., **1**).[5] However, the yields of products attributed to addition of phenyllithium (30%) and methyllithium (7%) appear to have discouraged development of this process. No simple benzyl anion coordinated to Cr(CO)$_3$ has been prepared by addition to styrene or by any other route.[6] We are interested in the scope and limitations of the reaction because (a) it allows conversion of a simple arene complex (e.g., **1**) into a more elaborate one (e.g., **2**), (b) it may allow isolation and study of the coordinated benzyl anion (e.g., **3**),[6] and (c) overall, two new carbon–carbon bonds (e.g., in **4**) could be formed, depending on the choice of nucleophile and electrophile in the reaction. We report that a variety of nucleophiles, electrophiles, and styrene-type ligands participate smoothly in the conversion represented. In the prototype example, 2-lithio-2-methylpropionitrile added to η^6-styrenechromium tricarbonyl slowly at −30 °C in THF, and quenching with ammo-



1: R_1=H
5: R_1=CH$_3$
6: R_1=SEt
3
2
4: R_1=H
8: R_1=CH$_3$
9: R_1=SEt

(1)

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(1) (a) For a recent report and leading references, see: M. F. Semmelhack and J. J. Harrison, *J. Org. Chem.*, **44**, 3275 (1979). (b) For a general review, see: G. Jaouen in "Application of Transition Metal Organometallics in Organic Synthesis", H. Alper, Ed., Academic Press, New York, Vol. 2, 1977.

(2) M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Barger, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, **101**, 3535 (1979).

(3) (a) G. Simmonneaux and G. Jaouen, *Tetrahedron*, **35**, 2249 (1979); (b) W. Trayhanovsky and R. J. Card, *J. Am. Chem. Soc.*, **94**, 2897 (1972).

(4) (a) G. Drehfahl, H. H. Horhold, and K. Kuhne, *Chem. Ber.*, **98**, 1826 (1965); (b) M. D. Rausch, G. A. Moser, E. L. Zaiko, and A. L. Lipman, *J. Organomet. Chem.*, **23**, 185 (1970). For an earlier report claiming styrenechromium tricarbonyl with a different mp, see: E. Mostardini, F. Calderazzo, and R. Ercoli, *Chim. Ind. (Milan)*, **42**, 1231 (1960).

(5) G. R. Knox, D. G. Leppard, P. L. Pauson, and W. E. Watts, *J. Organomet. Chem.*, **34**, 347 (1972).

(6) Related species have been characterized, but simple benzyl anions on Cr(CO)$_3$ have not been observed directly. For related examples, see: J. F. Helling and W. A. Hendrickson, *J. Organomet. Chem.*, **141**, 99 (1977). For species such as **3** as transient intermediates, see ref 3.

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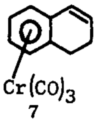
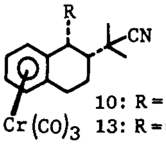
nium chloride (aqueous) after 3 h, produced complex **2** [$R_1 = C(CH_3)_2CN$, E = H] in 92% yield.

The results with four styrene complexes (**1**, **5**, **6**, and **7**) are summarized in Table I. The complexes were prepared by direct complexation of the syrene with chromium hexacarbonyl according to standard procedure (for **1**,[4] **6**,[7] and **7**[8]), or by an indirect procedure involving metalation of benzenechromium tricarbonyl, reaction with acetone, and elimination of water (for **5**).[9,10] The general procedure for nucleophilic addition/electrophilic trapping involved adding the styrene complex to a solution of the nucleophile in tetrahydrofuran at −78 °C and allowing the mixture to warm to 0 or 25 °C; then the electrophile was added, producing a stable complex (i.e., **2**) which was generally decomposed in excess iodine or ceric ammonium nitrate to afford the free arene. The anion of diethyl malonate failed to add to **1** while the lithium enolate anion from *tert*-butylmethyl ketone gave 10% of the expected adduct and no other products. With 2-lithio-1,3-dithiane, reaction with **1**, **5**, and **7** occurred, but the simple products from addition to the styrene terminus were not detected; however, the dithiane anion and other organolithium reagents add reasonably well to the α-(ethylthio)styrene complex (**6**, entries 11–14). The intermediate benzyl anions (**3**) are currently under study; the simple example of **3** with R_1 = H and $R_2 = C(CH_3)_2CN$ is stable at 25 °C for many hours. The α-methyl substituent in **5** led to somewhat lower efficiency in the overall process (entries 7 and 8), but it is not yet clear whether this is due to kinetic or thermodynamic effects. the α-(ethylthio) substituent has a beneficial effect in general.

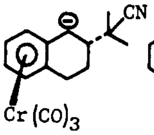
The dihydronapthalene complex **7** provides an example of the excellent stereochemical control in reactions of rings fused to arene–$Cr(CO)_3$ complexes.[12] Reaction with 2-lithio-2-methylpropionitrile proceeded rapidly at 0 °C; addition of saturated aqueous ammonium chloride solution followed by oxidative decomposition with ceric ammonium nitrate solution gave the adduct **12** as a colorless oil in 95–100% yield after short-path distillation [50 °C (0.001 torr)]. The intermediate complex **10** [E = H, R = $C(CH_3)_2CN$] can be isolated before the oxidation step, as a yellow solid with mp 158–159 °C, in 81% yield. Reaction of a solution of anion **11** with excess methyl iodide at −78 °C (warming slowly to 0 °C over 0.5 h) produced a mixture of complexes **7**, **10**, and **13** in a ratio of 1:2:6. Complete separation of **10** and **13** by chromatography was not achieved, but oxidation of the mixture followed by chromatographic purification provided the 1,2-disubstituted tetralin **14** as a colorless oil in 65% yield. The product is homogeneous (TLC, ^{13}C NMR) and is assigned the cis orientation, based on detailed analysis of the ^1H NMR spectral data,[13] and the well-established tendency for exo attack in the reactions of rigid bicyclic arene–$Cr(CO)_3$ complexes.[12]



7



10: R = H
13: R = CH_3



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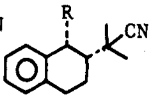
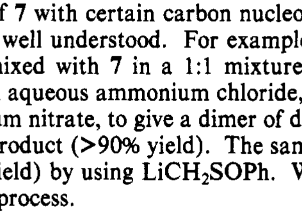


12: R = H
14: R = CH_3
15: R = COPh

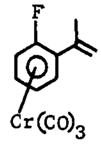


13

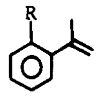
Further studies on **10** and **11** brought out limitations which may have general significance. Trapping of **11** with benzoyl chloride afforded an adduct (after oxidation) in only 32% yield which is assigned structure **15** (stereochemistry not determined), and other carbon electrophiles were less successful. Acetyl chloride, for example, gave only **10** in high yield under a variety of conditions, presumably via proton delivery. Formaldehyde and chloromethyl methyl ether gave low yields (<15%) of the expected adducts. The efficiency of reaction with methyl iodide was unexpectedly dependent on reaction temperature. When methyl iodide was added to a solution of **4** at 25 °C, rapid reaction ensued to produce 2,2-dimethylpropionitrile and the starting complex, **7**. Reaction at 0 °C gave a 1:1 mixture of **10** and **13**. We interpret these results in terms of a mobile equilibrium between **7** and **11** in the presence of $LiC(CH_3)_2CN$, heavily favoring **11** (essentially quantitative formation of **12** by quenching with ammonium chloride at −78, 0, and 25 °C). Then at −78 °C, reaction of the equilibrium mixture favored methylation of **11** (to give **13**) while at 25 °C the reverse reaction was fast enough to allow selective methylation of $LiC(CH_3)_2CN$ (to regenerate **2**).

Reactions of **7** with certain carbon nucleophiles gave results which are not well understood. For example, *tert*-butyl lithioacetate was mixed with **7** in a 1:1 mixture of THF/HMPA, quenched with aqueous ammonium chloride, and oxidized with ceric ammonium nitrate, to give a dimer of dihydronaphthalene as the major product (>90% yield). The same product was obtained (88% yield) by using $LiCH_2SOPh$. Work is in progress to define this process.

The complex **16** of *o*-(2-propenyl)fluorobenzene (**17**) was prepared by the sequence metalation of (fluorobenzene)chromium tricarbonyl,[10] quenching with acetone, and acid-promoted dehydration. Reaction of **16** with $LiC(CH_3)_2CN$ occurred slowly. Quenching with ammonium chloride after 2.5 h at 0 °C followed by ceric oxidation produced **17** (90% recovery), but after reaction for 5 h at 25 °C the quenching procedure gave **18** in 76% yield. No evidence for addition to the olefin unit was obtained.



16



17: R = F
18: R = $C(CH_3)_2CN$

Acknowledgment. We thank the National Science Foundation for generous support of this work and Dr. Charles Shuey (National Institutes of Health Postodctoral Fellow, 1978–1980) for data included in Table I and preliminary experimental work connected with this project.

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(7) Complex **6** was prepared by heating α-(ethylthio)styrene with chromium hexacarbonyl in dioxane at reflux under argon with an air condenser.[2] It was characterized by ^1H NMR, IR, mass spectroscopy, and combustion analyses (Supplementary Material).

(8) Complex **7** was obtained in 78% yield by heating 1,2-dihydronaphthalene with chromium hexacarbonyl in dioxane at reflux under argon for 40 h with an air condenser. It was recrystallized from a mixture of ether/hexane to give yellow crystals of mp 107–108 °C. The only previous literature report described an oil: H. Falk, K. Schlogel, and W. Steyer, *Monatsh. Chem.*, **97**, 1029 (1966). Full characterization appears in the supplementary material.

(9) Complex **5** has been obtained by direct reaction of α-methylstyrene with chromium hexacarbonyl, but the indirect procedure[10] is generally more efficient (yields of 95–98%) for substituted styrene complexes.

(10) M. F. Semmelhack, J. Bisaha, and M. Czarny, *J. Am. Chem. Soc.*, **101**, 768 (1979).

(11) For an earlier characterization of complex **5**, see: (a) R. C. Pruett, J. E. Wyman, D. R. Rink, and L. Parts, U.S. Patent 3 378 589; (b) *Chem. Abstr.*, **69**, 77512 (1968).

(12) For examples, see: M. A. Boudeville and H. des Abbayes, *Tetrahedron Lett.*, 2727 (1975).

(13) The evidence for the cis stereochemistry in **14** rests primarily on a coupling constant of 4.0 Hz for the protons at C-1 and C-2. Inspection of molecular models indicates that the reasonable conformation for the corresponding trans isomer would show a coupling larger than 7 Hz for the same protons, using the Karplus relation for vicinal proton–proton coupling.

Supplementary Material Available: Full characterization data for products listed in Table I, for compounds **12**, **14**, **15**, **17**, and **18**, and for complexes **5**, **6**, **7**, and **16** are available (8 pages). Ordering information is given on any current masthead page.[14,15]

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(14) Fellow of the J. S. Guggenheim Foundation, 1978-1979.

(15) Fellow of the DAAD (West Germany), 1978-1979.

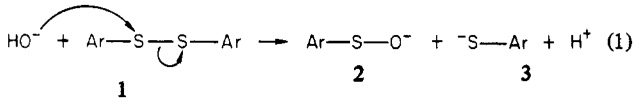
M. F. Semmelhack,*[14] Walter Seufert,[15] Leonard Keller
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received May 15, 1980

Oxidative Decomposition of a Mononitrobenzenesulfenate Ion in 15.3 M Potassium Hydroxide via a Stable Meisenheimer Complex

Sir:

A sulfenate ion, 3-carboxylato-4-nitrobenzenesulfenate (ArSO⁻, **2**), is formed quantitatively by attack of hydroxide ion on the aromatic disulfide, 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent, ArSSAr, **1**) in 3.0 M NaOH at 25 °C as shown in eq 1.[1] Under these conditions, the red sulfenate ion (**2**) is stable



$$\underset{\mathbf{1}}{HO^- + Ar{-}S{-}S{-}Ar} \longrightarrow \underset{\mathbf{2}}{Ar{-}S{-}O^-} + \underset{\mathbf{3}}{^-S{-}Ar} + H^+ \quad (1)$$

except for slow oxidation by O_2 to give the corresponding colorless sulfinate ion ($ArSO_2^-$).[1a] We report here an oxidative loss of sulfur from the sulfenate ion **2** in concentrated alkali (15.3 M KOH). Further, these experiments provide the first example of a stable Meisenheimer complex of a *mononitro* derivative of benzene.[2]

The reaction of hydroxide ion with the disulfide **1** [6.1 × 10^{-5} M] to produce the sulfenate **2** (eq 1) has a calculated half-life of ~0.1 s in 15.3 M KOH at 25 °C.[1b] However, under these conditions, the initial red color due to the sulfenate ion **2** fades within 10 s, and the absorbance of the product mixture in the region ~400-450 nm increases for many minutes; eventually, a stable final spectrum is obtained. The thiophenoxide ion (**3**, eq 1) is stable under these conditions, and subtraction of its absorption spectrum (Figure 1A) from that of the final product mixture produces a difference spectrum (Figure 1B) with a λ_{max} of 425 ± 2 nm. This spectrum identifies the major product of decomposition (64%) of the sulfenate **2** as 3-carboxylato-4-nitrophenoxide ion (**4**, Scheme I), by comparison with the spectrum of an authentic sample (Figure 1C).[3] A similar yield of sulfite ion was obtained.[4] A minor product with a λ_{max} of 475 nm is also formed (Figure 1D).

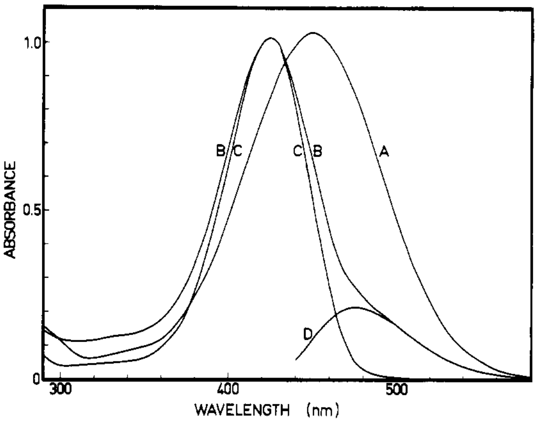


Figure 1. Final products of decomposition of 6.1 × 10^{-5} M 5,5′-dithiobis(2-nitrobenzoic acid) (**1**) in 15.3 M KOH at 25 °C. Oxygen was supplied as described in Figure 2. (A) Spectrum of 6.1 × 10^{-5} M 3-carboxylato-4-nitrothiophenoxide ion (**3**). (B) Calculated difference spectrum (final reaction mixture less spectrum A). (C) Spectrum of 3.9 × 10^{-5} M 3-carboxylato-4-nitrophenoxide ion (**4**). (D) Calculated difference spectrum (spectrum B less spectrum C).

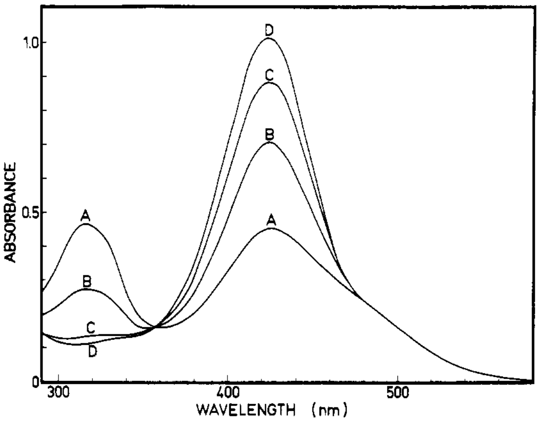
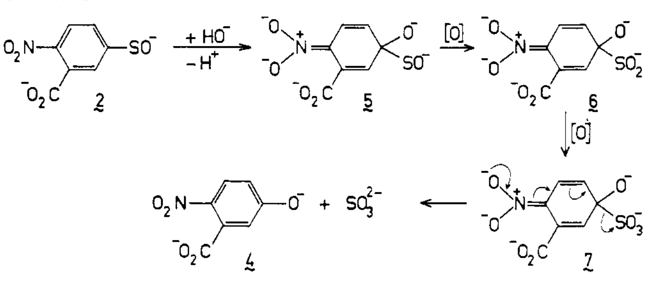


Figure 2. Formation of 3-carboxylato-4-nitrophenoxide ion (**4**) from 6.1 × 10^{-5} M 5,5′-dithiobis(2-nitrobenzoic acid) (**1**) in 15.3 M KOH at 25 °C. Calculated difference spectra [reaction mixture less 6.1 × 10^{-5} M 3-carboxylato-4-nitrothiophenoxide ion (**3**), (Figure 1A)]. (A) Scanned at 1.5-4.5 min. (B) Scanned at 9-12 min. (C) Scanned at 17-20 min. (D) Scanned at 60 min (Figure 1B). The solution was bubbled with O_2 for 3 min after scan A and after scan B and for a total of 15 min between scans C and D.

Scheme I



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(1) (a) Blakeley, R. L.; Riddles, P. W.; Zerner, B. *Phosphorus Sulfur* **1980**, in press. (b) Riddles, P. W.; Blakeley, R. L.; Zerner, B. *Anal. Biochem.* **1979**, *94*, 75-81.

(2) (a) Crampton, M. R. *Adv. Phys. Org. Chem.* **1969**, *7*, 211-257. de Boer, Th. J.; Dirkx, I. P. "The Chemistry of the Nitro and Nitroso Groups"; Zeuer, H., Ed.; Interscience: New York, 1970; Part 1, pp 487-612. Hall, T. N.; Poranski, C. F., Jr. *Ibid.* Part 2, pp 329-384. Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667-712. (b) A transient Meisenheimer adduct of hydroxide ion with a mononitro derivative of benzene occurs in the quantitative conversion of 2-nitrobenzoic acid to 2-nitroso-5-hydroxybenzoic acid in 15.8 M KOH: Treston, A.; Blakeley, R. L.; Zerner, B. *J. Chem. Soc., Chem. Commun.* **1980**, 394-395. (c) The crystalline triethylammonium salt of the 1,1-Meisenheimer complex of diethyl malonate carbanion with 2,4-dinitro-1-fluorobenzene is stable in dry DMF (λ_{max} 510 nm) but decomposes rapidly in the presence of water to give diethyl 2-(2,4-dinitrophenyl)malonate: Baudet, P. *Helv. Chim. Acta* **1966**, *49*, 545-551. In alkaline 70% Me_2SO-30% water, *N*,*N*′-dimethyl-*N*-(2,4-dinitrophenyl)ethylenediamine is in a rapidly attained equilibrium with its corresponding spiro Meisenheimer complex [λ_{max} 525 nm (ϵ_{max} 2.1 × 10^4 M^{-1} cm^{-1})]: Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1975**, *97*, 7458-7466.

(3) Species **4** was prepared as the free acid by Ag_2O oxidation of 2-nitro-5-hydroxybenzaldehyde and recrystallized from toluene, ethylene dichloride, and dilute HCl to give off-white crystals: mp 169.5-171 °C dec, lit. (Beyer, P. H. *Recl. Trav. Chim. Pays-Bas* **1921**, *40*, 621-631) mp 171.5-172 °C: *m/e* 183 ($M^{+\cdot}$, 32%); pK_a' 6.98; λ_{max} (nm), ϵ_{max} (M^{-1} cm^{-1}) at 25 °C: 0.1 M NaOH (397.5, 1.73 × 10^4), 10 M LiCl/0.1 M NaOH (399.5, 1.67 × 10^4), 3.1 M KOH (402, 1.84 × 10^4), 10 M NaOH (411, 2.06 × 10^4), 15.8 M KOH (425, 2.59 × 10^4). The identity of the final reaction product as **4** was confirmed by the spectral shift which occurred when KOH in the product mixture was diluted from 15.3 to 3.1 M.

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