Triplet Ground States of 4-Substituted 1,8-Naphthoquinodimethanes

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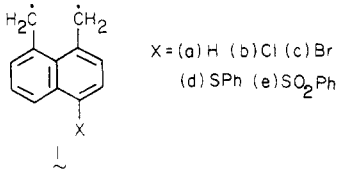
Photolysis of (5-substituted-8-methyl-1-naphthyl)diazomethanes in rigid glasses at 77 K leads to the triplet ESR spectra of the 4-substituted 1,8-naphthoquinodimethane biradicals. The substituents are X = H, Cl, Br, SPh, and SO_2Ph. A study of the temperature dependence of the biradical ESR spectra below 77 K demonstrated that these species were all ground-state triplets.

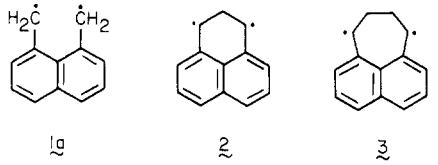
Introduction

A simple Hückel molecular orbital calculation of 1,8-naphthoquinodimethane **1** reveals that this 12 electron π



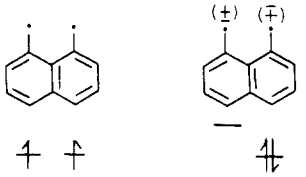
system possesses two nonbonding MO's in addition to five bonding and five antibonding MO's.[2] The Aufbau procedure requires that two electrons be distributed into the two NBMO's. The extension of Hund's first rule to molecules predicts that **1a** should have a ground-state triplet multiplicity.[3]

The HMO prediction is in agreement with PMO theory[4] and the "disjoint orbital" analysis of Border and Davidson.[5] Initial ESR studies of **1–3** were interpreted to favor singlet



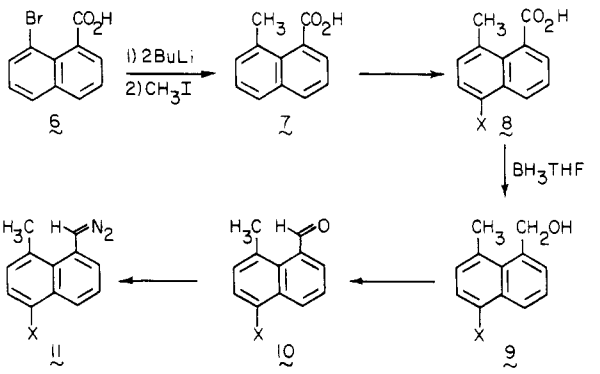
ground states for these compounds but later work demonstrated that the triplet was indeed the ground state.[6,7] Simple theory gave the correct answer despite the fact that **1** is almost certainly nonplanar due to steric interactions between the exocyclic methylenes.

A substituent on the aromatic ring is expected to lift the degeneracy of the NBMO's. If the substituent is either strongly electron donating or electron withdrawing the 1,8-NQM might be a zwitterionic singlet rather than a biradical. Hoffman has suggested that if δ (the energy



separation between the two formerly NBMO's) is greater than 1.5 eV the compound will be a ground-state singlet.[8]

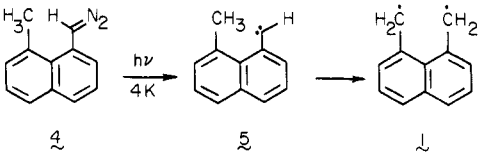
Scheme I[a]



[a] a, X = H; b, X = Cl; c, X = Br.

Results and Discussion

To study the effect of various substituents on the ground-state multiplicity of 1,8 NQM's we synthesized a series of (5-substituted-8-methyl-1-naphthyl)diazomethanes. Previous work in this laboratory has shown that photolysis of (8-methyl-1-naphthyl)diazomethane **4** at 4 K produces an intense ESR spectrum of 1,8-NQM (**1**). It



is not known whether carbene **5** is an intermediate in the formation of **1** as it was not detected at 4 K. Conceivably the hydrogen atom transfer may occur in an excited state of the diazo compound **4**, bypassing the carbene altogether.

The previous synthesis of **4** is somewhat tedious, a superior method starts with 8-bromo-1-naphthoic acid (**6**). Addition of a THF solution of **6** to excess *n*-butyllithium in THF at 195 K produces a dianion which can be quenched with methyl iodide to give 8-methyl-1-naphthoic acid (**7**). Acid **7** can be readily converted to 8-methyl-1-naphthaldehyde **10a** and then to diazo compound **4** by standard methods. Alternatively the methyl acid **7** can be halogenated and then carried through to the corresponding (5-halo-8-methyl-1-naphthyl)diazomethane (Scheme I). Chlorination and bromination worked well with elemental halogen in acetic acid. The 5-bromo-8-methyl-1-naphthoate **1i** was readily converted to thiophenyl ester **13** which was used to prepare diazo compounds **16** and **19** as shown in Scheme II.

Degassed solutions of diazo compounds **11a–c**, **16**, and **19** in 2-methyltetrahydrofuran were immersed in liquid nitrogen in a suprasil quartz dewar. The dewar was pos-

(1) Fellow of the A. P. Sloan Foundation and Camille and Henry Dreyfuss Teacher-Scholar.

(2) Coulson, C. A.; Streitwieser, A., Jr. "Dictionary of π Electron Calculations", W. H. Freeman: San Francisco, 1965.

(3) Hund, F. "Linienspektren und periodisches System der Elemente"; Springer-Verlag: Berlin, 1927, p 124.

(4) Platz, M. S. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982.

(5) Border, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(6) (a) Watson, C. R., Jr.; Pagni, R. M.; Dodd, J. R.; Bloom, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 2551. (b) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972. (c) Muller, J. F.; Muller, D.; Dewey, H.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629.

(7) (a) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216. (b) Platz, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3398.

(8) Hoffman, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

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Scheme II

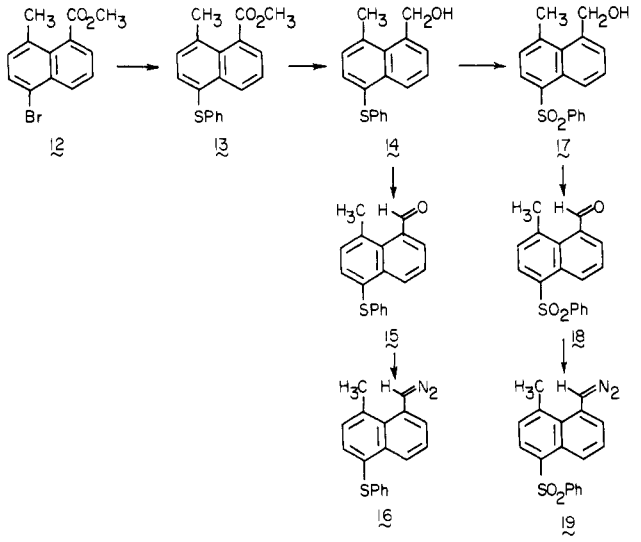
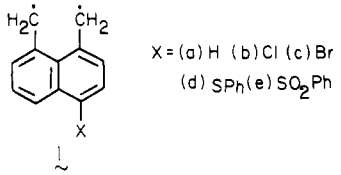


Table I. Zero Field Parameters of Substituted 1,8-Naphthoquinodimethane Biradicals at 77 K

substituent	$\|D/hc\|$, cm^{-1}	$\|E/hc\|$, cm^{-1}
H[6,7a]	0.0218	0.0021
Cl[9,c]	0.0215	0.0008
Br[a,c]	0.0269	0.0015
SC_6H_5[b,d]	0.0215	0.0007
$SO_2C_6H_5$[b,d]	0.0215	0.0006

[a] C_6F_6. [b] 2-Methyltetrahydrofuran. [c] Temperature range of Curie analysis is 24–80 K. [d] Temperature range of Curie analysis is 30–60 K.

itioned in the probe of an ESR spectrometer and briefly irradiated to generate new ESR signals which are stable at 77 K. The spectra (Figure 1) are characteristic of triplet biradicals and are assigned to a **1a–e**. The spectra were



readily analyzed in terms of their zero field-splitting (ZFS) parameters $|D/hc|$ and $|E/hc|$.[9] The ZFS parameters (Table I) show only minor variation with substituent. The signal intensities of biradicals **1a–e** were examined in the dark as a function of temperature. In all cases the simple form of the Curie Law (eq 1) was followed at low microwave power[9] (Figure 2).

$$IT = C \quad (1)$$

where I = signal intensity, T = temperature (K), and C is a constant. The strict observance of the Curie Law for biradicals **1a–e** means that these biradicals are either ground-state triplets or that the triplets are within a few cal/mol of the ground state. The electronic effect of the substituents is not sufficient to lower the energy of the zwitterionic form beneath that of the biradical in any of the compounds studied.

Experimental Section

All ESR measurements were made on a Varian E112 instrument. Variable temperature control was achieved by using an Oxford instrument. The signal intensities used in the Curie studies were the height of the ESR maxima. The zero field parameters were calculated by Wasserman's method, where $2D$ is the separation of the two outer peaks (in Gauss) and $6E$ is the separation of the two inner positive peaks. D and E can be converted into units of cm^{-1} by the conversion 10700 Gauss = 1 cm^{-1}.

8-Methyl-1-naphthoic Acid (7). Into a two-necked 500-mL flame-dried round-bottom flask equipped with a magnetic stirrer under a nitrogen atmosphere was placed 50 mL of freshly distilled THF (over sodium benzophenone). *n*-butyllithium was then syringed in slowly (1.65 m, 2.5 equiv, 61 mL) and the solution was cooled to 78 °C in a dry ice–acetone slush. 8-bromo-1-naphthoic acid (**6**) was dissolved in 100 mL of freshly distilled THF and was added slowly via an addition funnel to the cooled *n*-butyllithium–THF solution. The solution went from light yellow to a deep brown black after 5 min. Addition was complete after 1 h. The solution was then stirred for an additional 30 min and quenched with a large excess of methyl iodide (25 mL). This was slowly warmed up to room temperature and stirred for an additional 1 h at which point the solution went from deep black to a clear yellow-orange. This was then poured into ether (100 mL) and washed with 10% NaOH. The crude methyl acid was then

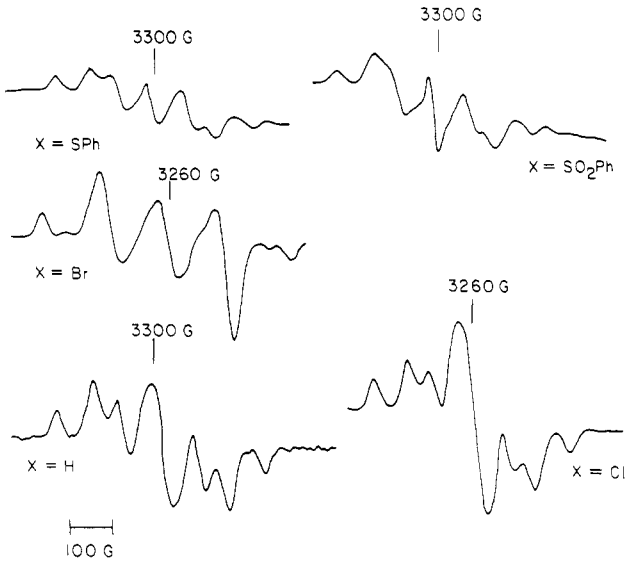


Figure 1. Triplet ESR spectra of biradicals **1a–f**.

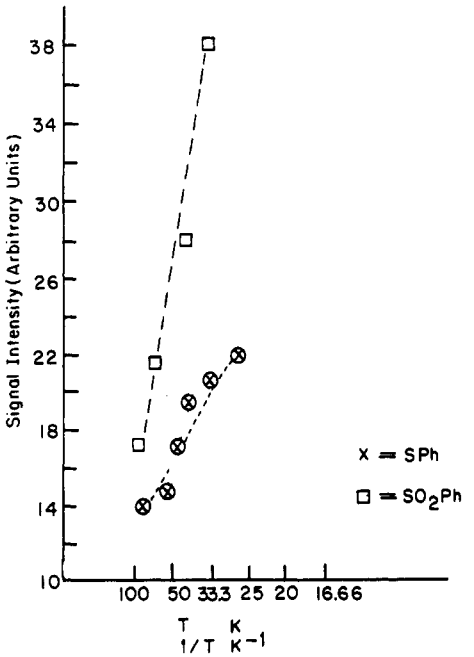


Figure 2. Representative Curie Weiss law plots obtained for substituted biradicals.

(9) (a) Breslow, R., Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112. (b) Wasserman, E.; Snyder, L. C.; Kager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

reprecipitated with concentrated hydrochloric acid, filtered, and dried. The yield of crude methyl acid was 7.35 g. To purify the methyl acid the product mixture was dissolved in ethanol (75 mL) and 2 mL of H_2SO_4 in a 100-mL round-bottom flask equipped with a condenser. The solution was refluxed for 9 h, cooled to room temperature, and poured into ether (100 mL). The ether extract was washed three times with 10% NaOH and the pure 8-methyl-1-naphthoic acid was reprecipitated with concentrated hydrochloric acid: yield (4.57 g) 61%; mp 151–152 °C (lit.[10] mp 152.2–153.2; NMR (acetone-d_6, δ) 2.65 (s, 3 H, methyl) 7.2–7.9 (m, 6 H, aromatic); MS, m/e calcd for $C_{12}H_{10}O_2$ 186.068, obsd 186.069.

5-Bromo-8-methyl-1-naphthoic Acid (8c). 8-Methyl-1-naphthoic acid (1.1 g, 0.006 mol) was dissolved in 25 mL of glacial acetic acid with stirring at room temperature. Bromine (0.948 g, 0.006 mol, 0.30 mL) was then added via pipet and an immediate orange color was imparted to the solution. This was then stirred in the dark for 18 h and the reaction was quenched by pouring the reaction mixture into 200 mL of water whereupon an immediate white precipitate was seen to form. This was filtered and dried in a dessicator giving 1.35 g (85%) of 5-bromo-8-methyl-1-naphthoic acid as a fine white powder: mp 196–198 °C; NMR (acetone-d_6, δ) 2.65 (s, 3 H, methyl), 7.2–7.8 (m, 4 H, aromatic H), 8.3–8.45 (d of d, 1 H, per H); MS, m/e calcd for $C_{12}H_9BrO_2$ 263.979, obsd 263.979.

5-Bromo-8-methyl-1-naphthalenemethanol (9c). Into a 50-mL two-necked flame-dried round-bottom flask with a magnetic stirrer, under a nitrogen atmosphere, equipped with a reflux condenser was placed 5-bromo-8-methyl-1-naphthoic acid (0.60 g, 0.0023 mol) with 20 mL of freshly distilled THF. Borane (4.5 mL 0.0045 mol, 1 M) was slowly syringed into the reaction vessel whereupon some frothing took place. The reaction mixture was refluxed for 9 h. The reaction was quenched by the slow addition of methanol and stirred at room temperature for 5 min. This was then poured into ether and washed three times with 10% sodium hydroxide to remove any unreacted acid. The organic phase was then washed two times with water and then with saturated sodium chloride. The ether phase was dried ($MgSO_4$) and the solvent removed in vacuo leaving a clear oil which solidified on standing to a white crystalline compound: yield 0.550 g (95%); mp 64–66 °C; NMR (acetone-d_6, δ) 2.65 (s, 3 H, methyl), 4.92 (s, 2 H, CH_2OH), 7.1–7.6 (m, 4 H, aromatic), 8.1–8.3 (d of d, 1 H, peri); MS, m/e calcd for $C_{12}H_{11}BrO$ 249.999, obsd 250.000.

5-Bromo-8-methyl-1-naphthalenecarboxaldehyde (10c). Pyridinium dichromate (0.80 g, 0.0021 mol) was added to a solution of 5-bromo-8-methyl-1-naphthalenemethanol (0.350 g, 0.0014 mol) in 70 mL of dichloromethane and the mixture was stirred for 6 h. The resulting dark brown solution was filtered over magnesium sulfate and the filtrate was evaporated to dryness. The residue was dissolved in diethyl ether, washed with 10% HCl and 10% $NaHCO_3$, and dried ($MgSO_4$). Removal of solvent under reduced pressure and recrystallization from ethanol gave 5-bromo-8-methyl-1-naphthalenecarboxaldehyde as fine light yellow crystals (0.302 g, 88%): mp 69–70 °C; NMR (acetone-d_6, δ) 2.65 (s, 3 H, methyl), 7.2–7.9 (m, 4 H, aromatic), 8.3–8.45 (d of d, 1 H, peri), 10.8 (s, 1 H); MS, m/e calcd for $C_{12}H_9BrO$ 247.984, obsd 247.984.

5-Bromo-8-methyl-1-naphthalenecarboxaldehyde *p*-Tosylhydrazone. (*p*-Tolylsulfonyl)hydrazide (0.60 g, 0.0032 mol) was added to 5-bromo-8-methyl-1-naphthalenecarboxaldehyde (0.240 g, 0.0010 mol) in ethanol and the mixture was refluxed for 1 h. The solution was cooled to room temperature to effect crystallization. Recrystallization from ethanol yielded 5-bromo-8-methyl-1-naphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (0.334 g, 83.4%) as white crystals: mp 172–173 °C; NMR (acetone-d_6, δ) 2.5 (s, 3 H, methyl (*p*-tosyl)), 2.65 (s, 3 H, methyl), 7.2–7.8 (m, 8 H, aromatic), 8.2–8.35 (d of d, 1 H, peri), 8.8 (s, 1 H, C=N).

(5-Bromo-8-methyl-1-naphthalenyl)diazomethane (11c). 5-Bromo-8-methylnaphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (0.167 g, 0.00040 mol) was dissolved in 10 mL of 30% KOH and 10 mL of *p*-dioxane and heated on a hot plate for 20 min. The resulting orange-red solution was poured into water (125 mL) and 30% KOH (25 mL). This was extracted two times with ether (75 mL) and the ethereal layer was dried (sodium sulfate). This solution was filtered and the solvent was removed in vacuo leaving an orange solid behind of (5-bromo-8-methylnaphthalenyl)diazomethane (0.080 g) 75%. The solution was dissolved in hexafluorobenzene and placed in a 4-mm quartz tube. The solution was then degassed, sealed, and stored in liquid nitrogen.

5-Chloro-8-methyl-1-naphthoic Acid (8b). 8-Methyl-1-naphthoic acid (1.5 g, 0.0081 mol) was dissolved in glacial acetic acid (20 mL) with stirring. A solution of chlorine gas (10 mL) dissolved in glacial acetic acid (3.4 g, 0.048 mol, 50 mL) was added dropwise over 30 min. The resulting solution was then stirred for 12 h. The reaction was quenched by pouring into 250 mL of cold water whereupon an immediate white precipitate was seen to form. This was set in the refrigerator overnight to induce total crystallization. This was filtered and dried to yield 5-chloro-8-methyl-1-naphthoic acid (1.64 g, 92%) as a fine white powder: mp 147.5–149 °C; NMR (acetone-d_6, δ) 2.75 (s, 3 H, methyl), 7.3–7.95 (m, 4 H, aromatic), 8.3–8.45 (d of d, 1 H, peri); MS, m/e calcd for $C_{12}H_9ClO_2$ 220.029, obsd 220.030.

5-Chloro-8-methyl-1-naphthalenemethanol (9b). 5-Chloro-8-methyl-1-naphthoic acid (1.0 g, 0.0048 mol) was reduced with borane–THF (1 M, 0.0091 mol, 10.7 mL) as per 8c: yield (0.85 g) 85%; mp 71–72 °C; NMR (acetone-d_6, δ) 2.9 (s, 3 H, methyl), 5.15 (s, 2 H, CH_2OH), 7.2–7.8 (m, 4 H, aromatic), 8.15–8.3 (d of d, 1 H, peri); MS, m/e calcd for $C_{12}H_{11}ClO$ 206.050, obsd 206.050.

5-Chloro-8-methyl-1-naphthalenecarboxaldehyde (10b). Pyridinium dichromate (1.3 g, 0.00345 mol) was added to a solution of 5-chloro-8-methyl-1-naphthalenemethanol (0.496 g, 0.0023 mol) in 100 mL of dichloromethane. The reaction was run as per that of **10c** to give 5-chloro-8-methyl-1-naphthalenecarboxaldehyde as fine white crystals (0.410 g, 83%): mp 77–79 °C; NMR (acetone-d_6, δ) 2.75 (s, 3 H, methyl), 7.25–7.9 (m, 4 H, aromatic), 8.3–8.5 (d of d, 1 H, peri), 10.8 (s, 1 H, aldehyde); MS, m/e calcd for $C_{12}H_9ClO$ 204.034, obsd 204.035.

5-Chloro-8-methyl-1-naphthalenecarboxaldehyde (*p*-Tolylsulfonyl)hydrazone. (*p*-Tolylsulfonyl)hydrazine (0.480 g, 0.00258 mol) was added to 5-chloro-8-methyl-1-naphthalenecarboxaldehyde (0.360 g, 0.0018 mol) in ethanol and the mixture was refluxed for 3 h. The solution was cooled to room temperature and the excess ethanol was removed under reduced pressure to yield a white-yellow crystalline compound. This was diluted with diethyl ether where a pure white crystalline compound was seen to form. This was filtered to yield 5-chloro-8-methyl-1-naphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (0.45 g 68%): mp 146–148 °C dec; NMR (acetone-d_6, δ) 2.5 (s, 3 H, *p*-tosyl CH_3), 2.7 (s, 3 H, methyl), 7.2–7.9 (m, 8 H, aromatic), 8.2–8.3 (d of d, 1 H, peri), 8.9 (s, 1 H, R*H*C=NN).

(5-Chloro-8-methyl-1-naphthalenyl)diazomethane (11c). 5-Chloro-8-methylnaphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (0.140 g, 0.000376 mol) was dissolved in 10 mL of 30% KOH and 10 mL of *p*-dioxane and heated on a hot plate for 20 min. The resulting orange-red solution was poured into 10% Na_2CO_3. This was extracted two times with ether (50 mL) and the ethereal layer was dried (sodium sulfate). The solution was filtered and the solvent was removed in vacuo leaving an orange oil of (5-chloro-8-methylnaphthalenyl)diazomethane (0.065 g, 75%). The oil was dissolved in hexafluorobenzene and placed in a 4-mm quartz tube. The solution was then degassed, sealed, and kept under liquid nitrogen.

5-Bromo-8-methyl-1-naphthoyl Chloride. 5-Bromo-8-methyl-1-naphthoic acid (1 g, 0.0038 mol) was dissolved with stirring and heating in thionyl chloride (15 mL) in a 50-mL round-bottom flask equipped with a reflux condensor. This was heated for 2.5 h and cooled to room temperature. The excess thionyl chloride was removed under reduced pressure leaving behind a brown oil. The product was not characterized but was used immediately in the next reaction.

Methyl 5-Bromo-8-methyl-1-naphthoate (12). 5-Bromo-8-methyl-1-naphthoyl chloride (1 g, 0.0035 mol) was dissolved with stirring in a 50-mL round-bottom flask containing methanol (20 mL) and equipped with a reflux condenser. The solution was refluxed for 8 h under a nitrogen atmosphere, cooled to room temperature, and poured into ether. The organic phase was

(10) Cason, J.; Wordle, J. D. *J. Org. Chem.* **1950**, *15*, 608.

washed with 10% NaOH and 5% HCl and dried with $MgSO_4$. Removal of solvent under reduced pressure yielded a yellow crystalline compound, methyl 5-bromo-8-methyl-1-naphthoate (0.77 g): 87%; mp 53–56 °C; IR (mull, cm^{-1}) 1750 (C=O, ester), 1210 (CH_3O), 1520, 980, 830, 770 (aromatic); NMR (acetone-d_6, δ) 2.5 (s, 3 H, methyl), 3.85 (s, 3 H, methyl ester), 7.1–7.8 (m, 4 H, aromatic), 8.20–8.45 (d of d, 1 H, peri); MS, m/e calcd for $C_{13}H_{11}BrO_2$ 279.140, obsd 279.141.

Methyl 5-(Phenylthio)-8-methyl-1-naphthoate (13). Methyl 5-bromo-8-methyl-1-naphthoate (0.74 g, 0.00265 mol) and cuprous phenylmercaptide (0.67 g, 0.004 mol) were dissolved in hexamethylphosphoric triamide (12 mL) and pyridine (0.2 mL). The stirred mixture was heated at 160 °C for 6 h under a nitrogen atmosphere. The mixture was cooled and poured into water with simultaneous cooling in an ice bath. The aqueous solution was extracted with ether. The organic solution was washed with diluted HCl, saturated $NaHCO_3$, and saturated NaCl solution. This was dried over anhydrous $MgSO_4$ and the solvent was removed to yield an oily brown liquid. The mixture was separated by MPLC to yield 0.49 g (60.3%) of methyl 5-(phenylthio)-8-methyl-1-naphthoate as a white crystalline compound: mp 75–77 °C; IR (neat, cm^{-1}) 1750 (C=O, ester), 1210 (CH_3O), 1510, 980, 830, 770 (aromatic); NMR (chloroform-d, δ) 2.55 (s, 3 H, methyl), 3.9 (s, 3 H, methyl ester), 7–7.8 (m, 9 H, aromatic), 8.45–8.65 (d of d, 1 H, peri); MS, m/e calcd for $C_{19}H_{16}SO_2$ 308.087, obsd 308.088.

5-(Phenylthio)-8-methyl-1-naphthalenemethanol (14). Methyl 5-(phenylthio)-8-methyl-1-naphthoate (0.60 g, 0.002 mol) was dissolved in 15 mL of THF and placed in an addition funnel. Lithium aluminum hydride (0.0630 g, 0.0016 mol) was placed in a three-neck 50-mL flame-dried round-bottom flask equipped with a mechanical stirrer, a condenser, and an addition funnel under a nitrogen atmosphere. The lithium aluminum hydride was dissolved in 10 mL of freshly distilled THF. To this was added the ester solution slowly and the mixture was refluxed for 12 h. The solution was quenched with isopropyl alcohol and water. The solution was stirred with 2 M sulfuric acid solution for 15 min and extracted with ether. The organic phase was dried over $MgSO_4$ and the solvent was removed to yield 0.46 g (84.4%) of [5-(phenylthio)-8-methyl-1-naphthalenyl]methanol as crystalline white solid: mp 59–61 °C; IR (neat, cm^{-1}) 3000–3350 (broad, OH), 1520, 1200, 1000, 830, 770 (aromatic); NMR (acetone-d_6, δ) 2.7 (s, 1 H, OH), 3.0 (s, 3 H, methyl), 5.1 (s, 2 H, CH_2OH), 7.05–7.8 (m, 9 H, aromatic), 8.25–8.50 (d of d, 1 H, peri); MS, m/e calcd for $C_{18}H_{16}SO$ 280.092, obsd 280.093.

5-(Phenylthio)-8-methyl-1-naphthalenecarboxaldehyde (15). A solution of CH_2Cl_2 (4 mL) and oxalyl chloride (0.15 mL, 1.65 mmol) was placed in a 50-mL four-neck round-bottom flask equipped with an overhead mechanical stirrer and two pressure equilizing dropping funnels containing Me_2SO (0.27 mL, 3.38 mmol) dissolved in CH_2Cl_2 (1 mL) and the alcohol **14** (0.4 g, 1.4 mmol) in CH_2Cl_2, respectively. The Me_2SO was added to the stirred oxalyl chloride solution at −78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 5 min and then the alcohol was added within 5 min. Stirring was then continued for an additional 15 min. Triethylamine (2.2 mL, 15.62 mmol) was added and the reaction mixture stirred for 15 min and allowed to warm to room temperature. Water was added and the aqueous layer was reextracted with additional CH_2Cl_2. The organic layers were combined, washed with saturated NaCl solution, dilute HCl, and water. The organic solution was dried with anhydrous Na_2SO_4 and the solvent was removed in a rotary evaporator. Recrystallization from ethanol yields 0.35 g (88.2%) of 5-(phenylthio)-∞8-methyl-1-naphthalenecarboxaldehyde as a white crystalline solid: mp 80–82 °C; IR (mull, cm^{-1}) 1680 (C=O, aldehyde), 1500, 1200, 1030, 820 770 (aromatic); NMR (acetone-d_6, δ) 2.6 (s, 3 H, methyl), 7.05–7.85 (m, 9 H, aromatic), 8.45–8.65 (d of d, 1 H, peri), 10.85 (s, 1 H, CHO); MS, m/e calcd for $C_{18}H_{14}SO$ 278.077, obsd 278.077.

5-(Phenylthio)-8-methyl-1-naphthalenecarboxaldehyde (*p*-Tolylsulfonyl)hydrazone. (*p*-Tolylsulfonyl)hydrazide (0.636 g, 0.0034 mol) was added to 5-(phenylthio)-8-methyl-1-naphthalenecarboxaldehyde (0.22 g, 0.0008 mol) in ethanol and the mixture was refluxed for 1 h. The solution was cooled to room temperature to effect crystallization. Recrystallization from ether yielded 5-(phenylthio)-8-methyl-1-naphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (0.263 g, 74.5%) as white crystals: mp 93–95 °C; IR (mull, cm^{-1}) 3300 (NH), 1320, 1170 (SO_2), 1600, 1450, 940, 820 (aromatic); NMR (acetone-d_6, δ) 2.5 (s, 3 H, *p*-tosyl CH_3), 2.7 (s, 3 H, methyl), 7.2–7.9 (m, 13 H, aromatic), 8.2–8.3 (d of d, 1 H, HC=NN).

[5-(Phenylthio)-8-methylnaphthalenyl]diazomethane (16). 5-(Phenylthio)-8-methylnaphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (30 mg, 0.067 mmol) was dissolved in 5 mL of 30% KOH and 5 mL of 2-methyltetrahydrofuran and heated on a hot plate for 10 min. The organic orange-red solution was filtered and dried with anhydrous sodium sulfate. The solvent was removed in vacuo leaving an orange solid behind of [5-(phenylthio)-8-methylnaphthalenyl]diazomethane: IR (neat, cm^{-1}) 2060 (C=N_2). It was dissolved in 2-methyltetrahydrofuran and placed in a 4-mm quartz tube. The solution was then degassed, sealed, and kept under liquid nitrogen.

5-(Phenylsulfonyl)-8-methylnaphthalenemethanol (17). To a cooled solution of 0.20 g (0.0007 mol) of 5-(phenylthio)-8-methyl-1-naphthalenemethanol (**14**) in 5 mL of glacial acetic acid was added 0.30 mL (0.09 g, 0.0027 mol) of 30% hydrogen peroxide. This mixture was heated for 2 h on a steam plate and cooled to room temperature. A slightly yellow solid formed when the solution was poured into ice water which was dissolved in CH_2Cl_2. The solution was washed with 10% NaOH and dried with anhydrous Na_2SO_4 and the solvent was removed in a rotovap. Recrystallization from ethanol gave a slightly yellow crystalline compound 0.16 g (70%): mp 138–140 °C; IR (KBr, cm^{-1}) 3200–3550 (broad, OH), 1310, 1160 (SO_2), 1510, 1220, 960, 815, 770 (aromatic); NMR (chloroform-d, δ) 2.9 (s, 3 H, methyl), 5.55 (s, 2 H, CH_2OH), 7.2–8.0 (m, 9 H, aromatic), 8.3–8.8 (d of d, 1 H, peri); MS, m/e calcd for $C_{18}H_{16}SO_3$ 312.082, obsd 312.082.

5-(Phenylsulfonyl)-8-methyl-1-naphthalenecarboxaldehyde (18). A solution of CH_2Cl_2 (5 mL) and oxalyl chloride (0.20 mL, 2.2 mmol) was placed in a 50-mL three-neck round-bottom flask equipped with an overhead mechanical stirrer and two pressure equilizing dropping funnels containing Me_2SO (0.32 mL, 4.4 mmol) dissolved in CH_2Cl_2 (1 mL) and the alcohol **17** (0.58 g, 1.86 mmol) in 2 mL of CH_2Cl_2, respectively. The Me_2SO was added to the stirred oxalyl chloride solution at −78 °C. The reaction mixture was stirred for 5 min and then the alcohol was added within 5 min. Stirring was continued for an additional 15 min. Triethylamine (1.3 mL, 9.3 mmol) was added and the reaction mixture stirred for 5 min and then allowed to warm to room temperature. Water was then added and the aqueous layer was reextracted with additional CH_2Cl_2. The organic layers were combined and washed with saturated NaCl solution, dilute HCl, and water. The organic solution was dried with anhydrous Na_2SO_4 and the solvent was removed in a rotary evaporator. Recrystallization from methanol yielded a white solid (0.45 g, 78.1%): mp 206–208 °C; IR (mull, cm^{-1}) 1680 (aldehyde C=O), 1310, 1160 (SO_2), 1510, 1220, 960, 820, 770 (aromatic); NMR (chloroform-d, δ) 2.7 (s, 3 H, methyl), 7.25–7.9 (m, 9 H, aromatic), 8.3–9.0 (d of d, 1 H, peri), 10.7 (s, 1 H, CHO); MS, m/e calcd for $C_{18}H_{14}SO_3$ 310.066, obsd 310.067.

5-(Phenylsulfonyl)-8-methyl-1-naphthalenecarboxaldehyde (*p*-Tolylsulfonyl)hydrazone. (*p*-Tolylsulfonyl)hydrazine (1.29 g, 0.00694 mol) was added to 5-(phenylsulfonyl)-8-methyl-1-naphthalenecarboxaldehyde (0.50 g, 0.00163 mol) in ethanol and the mixture was refluxed for 1 h. The solution was cooled to room temperature to effect crystallization. Recrystallization from ether yielded 5-(phenylsulfonyl)-8-methyl-1-naphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (0.584 g, 76%) as white crystals: mp 188–190 °C; IR (mull, cm^{-1}) 3200 (NH), 1600, 1450, 940, 895, 820, 760 (aromatic), 1320, 1170 (SO_2); NMR (chloroform-d, δ) 2.5 (s, 3 H, *p*-tosyl CH_3), 2.7 (s, 3 H, methyl), 7.2–7.9 (m, 13 H, aromatic), 8.2–8.3 (d of d, 1 H, peri), 8.9 (s, 1 H, HC=NN).

[5-(Phenylsulfonyl)-8-methyl-1-naphthalenyl]diazomethane (19). 5-(Phenylsulfonyl)-8-methyl-1-naphthalenecarboxaldehyde (*p*-tolylsulfonyl)hydrazone (30 mg, 0.063 mmol) was dissolved in 5 mL of 30% KOH and 2 mL of 2-methyltetrahydrofuran and heated on a hot plate for 10 min. The organic orange-red solution was filtered and dried with anhydrous sodium sulfate. The solvent was removed in vacuo leaving an orange solid behind of [5-(phenylsulfonyl)-8-methylnaphthalenyl]diazomethane: IR (neat, cm^{-1}) 2060 (C=N_2). It was dissolved in

2-methyltetrahydrofuran and placed in a 4-mm quartz tube. The solution was then degassed, sealed, and kept under liquid nitrogen.

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Registry No. **1a**, 62617-73-6; **1b**, 91424-03-2; **1c**, 91424-04-3; **1d**, 91424-05-4; **1e**, 91424-06-5; **1f**, 91424-07-6; **6**, 1729-99-3; **7**, 19310-98-6; **8b**, 91424-13-4; **8c**, 91424-08-7; **8d**, 91424-19-0; **9b**, 91424-14-5; **9c**, 91424-09-8; **9d**, 91424-20-3; **10b**, 91424-15-6; **10b** (tosylhydrazone), 91424-16-7; **10c**, 91424-10-1; **10c** (tosylhydrazone), 91424-11-2; **10d**, 91424-21-4; **10d** (tosylhydrazone), 91424-22-5; **11b**, 91424-17-8; **11c**, 91424-12-3; **11d**, 91424-23-6; **12**, 91424-25-8; **13**, 91424-26-9; **14**, 91424-27-0; **15**, 91424-28-1; **15** (tosylhydrazone), 91424-29-2; **16**, 91424-30-5; **17**, 91424-31-6; **18**, 91424-32-7; **18** (tosylhydrazone), 91424-33-8; **19**, 91424-34-9; 5-(iodomercurio)-8-methyl-1-naphthoic acid, 91424-18-9; 5-bromo-8-methyl-1-naphthoyl chloride, 91424-24-7; cuprous phenymercaptide, 1192-40-1.

On the Conjugative Isomerizations of β,γ-Unsaturated Esters. Stereochemical Generalizations and Predictions for 1,3-Prototropic Shifts under Basic Conditions

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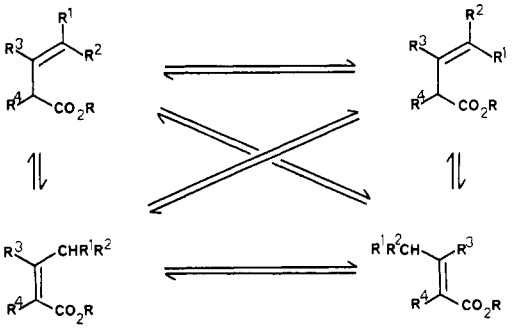
An investigation of the base-catalyzed conjugative isomerization of a series of β,γ-unsaturated esters to their corresponding α,β-unsaturated esters was performed. It was found that, with sodium hydride in THF, methyl 3-butenoate isomerized initially to a 5:1 ratio of (*Z*)- to (*E*)-methyl 2-butenoates; the *Z*:*E* ratio is time dependent, and after several days, the thermodynamic ratio 1:23 = *Z*:*E* was obtained. The isomerization appears to be catalytic in NaH, as it proceeds with less than 1 molar equiv of base, no hydrogen evolution is observed, and the reaction rate is approximately first order in NaH and zero order in ester. Under the same conditions (*Z*)-methyl 3-hexenoate isomerized stereoselectively to (*E*)-methyl 2-hexenoate while (*E*)-methyl 3-hexenoate isomerized to a 2:1 mixture of (*Z*)- and (*E*)-methyl 2-hexenoates. These product ratios are far from the isomeric compositions obtained under equilibrating conditions. To investigate further the stereochemical outcome of these isomerizations, three isomeric β,γ-unsaturated methyl esters were studied: (a) methyl 3-ethyl-3-butenoate isomerized exclusively to (*E*)-methyl 3-methyl-2-pentenoate; (b) (*E*)-methyl 3-methyl-3-pentenoate isomerzied exclusively to (*Z*)-methyl 3-methyl-2-pentenoate; (c) (*Z*)-methyl 3-methyl-3-pentenoate isomerized exclusively to (*E*)-methyl 3-methyl-2-pentenoate. In the latter three cases, dimerization was not observed presumably due to steric effects. Related results were observed for a smaller series of β,γ-unsaturated amide isomerizations. Examination of the literature on olefin isomerizations reveals a general trend that the current results exemplify. Thus, in the absence of severe steric factors or cation–anion complexation, deprotonation at allylic positions kinetically preferentially forms the anion possessing a cisoid crotyl subunit (if available) regardless of initial substrate conformation. The stereochemical consequences of this results in $E \rightarrow Z$ and $Z \rightarrow E$ geometry conversions in kinetic 1,2-transpositions of olefins. This generalization can also be applied to the stereochemical results of ketone, ester, and hydrazone enolate formation, base-catalyzed exchange in polysubstituted aromatics and heteroaromatics, and other reactions involving the formation of allylic or benzylic anions.

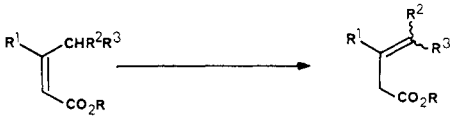
α,β- and β,γ-unsaturated esters play important roles in organic chemistry. The reactivity of these groups to both nucleophiles and electrophiles under a variety of reaction conditions has made them ideal precursors in many organic chemical syntheses, and numerous natural products possess these structural subunits.

While it is well-known that α,β- and β,γ-unsaturated esters can readily isomerize to each other under a variety of conditions,[1-3] there are significant gaps in our full understanding of the mechanistic basis of these reactions and also in our ability to control the course of the isomerizations. Most of the studies published to date,[2-4] and certainly the bulk of the early investigations,[1] deal with the *thermodynamic* equilibrium of these unsaturated esters

Scheme I



Scheme II



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