mixture of benzene, toluene, and anisole or with a mixture of benzene and chlorobenzene. The aromatic compounds were always in a large excess over **3b**. After the silver salts were filtered, the mixtures were analyzed by gas chromatography with chrysene as an internal standard. No correction for a possible different detector response for the different compounds was introduced. The relative reactivities at the para position of the aromatic compounds were calculated from the relative ratios of the starting materials and the para-substitution products after statistical correction for the presence of six identical positions in benzene; i.e., $\log(k_X/k_H) = \log (6[Ph_2C{=}C(An)C_6H_4X\text{-}p]/[Ph_2C{=}C(An)Ph]([C_6H_6]/[C_6H_5X])$. The reaction conditions and the data are given in Table III, and a Hammett plot of log (k_X/k_H) against σ^+ is given in Figure 1.

Isomer Distributions. The ortho/meta/para distribution of the substitution product in the reactions of **3b** was determined with the aid of authentic samples in most cases.

Reaction of **3b**/$AgBF_4$ with toluene gave only two peaks in the gas chromatographic analysis. However, by comparison with authentic samples of the substitution products which were obtained from the reactions of **3c,d,e** with anisole or from the main product isolated from the reaction of **3b** with toluene, it was found that the peaks due to the ortho and meta isomers overlap. Consequently, the distribution was determined by integration of the three separate methyl signals in the ^1H NMR spectrum in CCl_4.

In the reaction of **3b** with anisole the ortho and para isomeric products gave good separation on a OV-17 column at 240 °C. Their ratio was calculated by assuming an identical detector response. A sample of the meta isomer was not available for comparison, but on the assumption that the order of retention times of the isomers is similar to that of the methyl derivatives, no peak for the meta isomer was detected. NMR spectra showed the presence of the *o*-methoxy derivative in the reaction of the other compounds with anisole, in a low yield. No further investigation was conducted on the formation of the ortho isomer.

In the AgOTf-assisted reaction with chlorobenzene, the ortho/para isomer ratio was determined by VPC. There is some overlap between the two peaks, and hence the presence of a meta isomer (whose VPC behavior is unknown) can escape detection.

Reaction of Triphenylvinyl Bromide (3f) with $AgBF_4$ in Benzene. A mixture of **3f**, $AgBF_4$, 2,6-lutidine, and benzene was heated at 150 °C for 48 h in the manner described in the vinylation procedure. After workup of the reaction mixture, triphenylvinyl fluoride (mp 96–99 °C; 82%) was obtained by preparative VPC (column: OV-17, 1 m) and identified by comparison with an authentic sample (mp 103–104 °C).[32] Also, tetraphenylethene was formed in 8% yield.

Acknowledgment. Z.R. is indebted to Kyushu University for a visiting professorship during January–March 1981 and to Professor H. Taniguchi's group for their hospitality during this period.

Registry No. 3a, 25354-46-5; **3b**, 25354-48-7; **3c**, 83248-27-5; **3d**, 83248-28-6; **3e**, 83248-29-7; **3f**, 1607-57-4; **3g**, 40811-05-0; **3h**, 83248-30-0; **3i**, 5912-93-6; **5a**, 10019-24-6; **5b**, 68161-05-7; **5c**, 83248-31-1; **5d**, 83248-32-2; **5e**, 83248-33-3; **5f**, 70592-05-1; **5g**, 26957-36-8; **5h** (isomer 1), 54186-51-5; **5h** (isomer 2), 54186-52-6; **5i**, 83248-34-4; **6b**, 83248-35-5; **7f**, 632-51-9; **7i**, 781-33-9; **8b**, 83248-36-6; C_6H_5OMe, 100-66-3; C_6H_5Me, 108-88-3; C_6H_6, 71-43-2; C_6H_5Cl, 108-90-7; $AgBF_4$, 14104-20-2; AgOTf, 2923-28-6; ethyl *m*-tolylacetate, 40061-55-0; ethyl *o*-tolylacetate, 40291-39-2; bromobenzene, 108-86-1; 1,1-diphenyl-2-tolylethene, 83248-37-7; 1,1-diphenyl-2-*o*-tolylethene, 72292-01-4; 4'-methoxy-2,2-diphenylacetophenone, 1889-74-3; *o*-bromoanisole, 578-57-4; *p*-chlorophenyl bromide, 106-39-8; 1-(acetylamino)-1,2,2-tris(*p*-methoxyphenyl)ethene, 83248-38-8.

(32) Meier, R.; Böhler, F. *Chem. Ber.* **1957**, *90*, 2344.

Regiochemical Control in the Diels–Alder Reaction of Substituted Naphthoquinones. The Directing Effects of C-6 Oxygen Substituents

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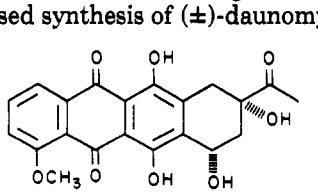
The Diels–Alder reactions of 6-hydroxy-, 6-methoxy-, and 6-acetoxynaphthoquinone with *trans*-1-methoxy-3-methyl-1,3-butadiene have been studied, and the regiochemistry of the adducts has been determined. The results are consistent with the hypothesis that the acetoxy (as well as the hydroxy and methoxy) substituent functions as an electron donor despite Hammett σ constants which would suggest otherwise.

In the course of studies leading to a regiospecific, Diels–Alder-based synthesis of (±)-daunomycinone (1),[2,3]



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the hypothesis was advanced that the regiochemical outcome of the reaction in eq 1[4] could be rationalized by considering the acetoxy group in **2** as an electron-donating substituent (assuming[4d] a polarized transition state). According to that rationale, resonance donation (**2**, arrows) from the acetoxy group into the C-4 carbonyl would render

(1) Recipient of NIH Career Development Award 1975–1980.

(2) (a) Kelly, T. R.; Gillard, J. W.; Goerner, R. N., Jr.; Lyding, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 5513. (b) Kelly, T. R. *Tetrahedron Lett.* **1978**, 1387.

(3) Kelly, T. R.; Vaya, J.; Ananthasubramanian, L. *J. Am. Chem. Soc.* **1980**, *102*, 5983.

(4) (a) Muxfeldt, H. *Angew. Chem.* **1962**, *74*, 825. Muxfeldt, H.; Haas, G.; Hardtmann, G.; Kathawala, F.; Mooberry, J. B.; Vedejs, E. *J. Am. Chem. Soc.* **1979**, *101*, 696. (b) Trost, B. M.; Ippen, J.; Vladuchick, W. C. *Ibid.* **1977**, *99*, 8116. Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *Ibid.* **1980**, *102*, 3548. (c) Stork, G.; Hagedorn, A. A., III. *Ibid.* **1978**, *100*, 3609. (d) For one discussion of the nature of the dipolar Diels–Alder transition state see the papers cited in ref 4b.

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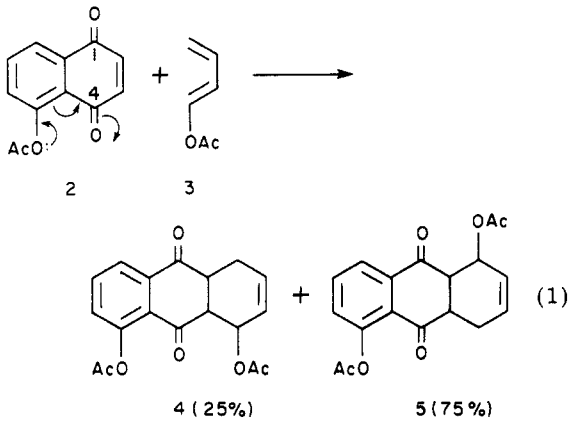


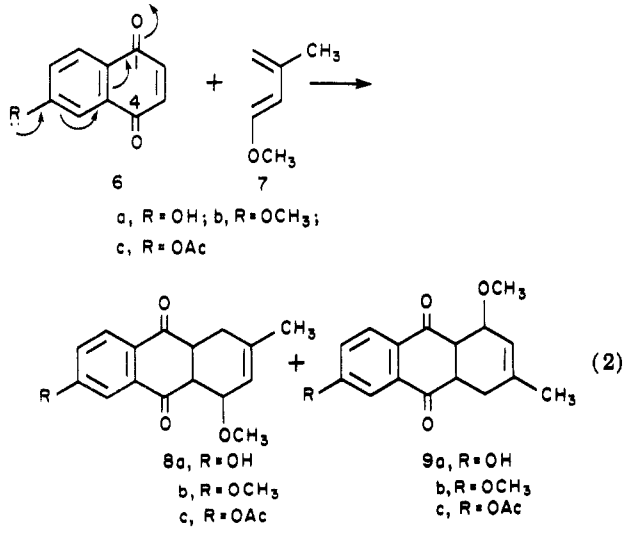
2 3

4 (25%) 5 (75%) (1)

(by default) the C-1 carbonyl the more electron deficient of the carbonyl substituents on the C_2–C_3 double bond, and hence the dominant regiochemical control element.[5] The regiochemical outcome (**4**/**5** ratio of 1:3)[4] of the reaction in eq 1 is consistent with that hypothesis.

While the above rationale has proven in practice to be a fruitful one,[2,3,6] it has nonetheless been argued that the basic premise (i.e., that acetoxy functions as an electron-donating substituent) is incorrect. This criticism is supported by Hammett σ constants,[7] according to which (Table I) acetoxy in contrast to hydroxy and methoxy is an electron-withdrawing substituent in *both* the meta and para positions.

In order to address the conflict between the hypothesis invoking electron donation from the acetoxy group and the Hammett constants, it was deemed worthwhile to examine the regiodirective role of acetoxy in a substrate different from **2**, since alternative explanations (e.g., a peri interaction in **2**) unique to the results in eq 1 may be suggested. To this end we have now examined the Diels–Alder reactions of the C-6-substituted naphthoquinones **6a–c** with **7** (eq 2; the methyl group was incorporated in **7** to facilitate



6 7

a, R = OH; b, R = OCH_3; c, R = OAc

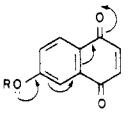
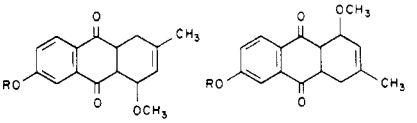
8a, R = OH; 9a, R = OH
b, R = OCH_3; b, R = OCH_3
c, R = OAc; c, R = OAc (2)

structure determination of the adducts, vide infra). Being para donors (**6**, arrows), the methoxy and hydroxy groups, according to the hypothesis,[2,3] should produce regioisomer **8** as the major product. If the acetoxy group also functions as an electron donor, **8c** would be predicted as the major product from the reaction of **6c** and **7**.

Table I[7]

substituent	σ_m	σ_p
OH	+0.12	−0.37
OCH_3	+0.12	−0.27
OAc	+0.39	+0.31

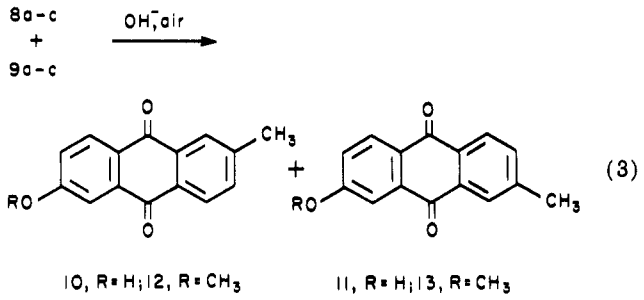
Table II

starting naphthoquinone	adducts[a]	
		
	8	9
6a, R = H	75	25
6b, R = CH_3	75	25
6c, R = Ac	60	40

[a] Ratios based on the composition of derived mixtures of **12** and **13**.[12]

Results and Discussion

Methods. Diels–Alder reactions of **6a–c** with **7** were conducted in acetone-d_6 at 25 °C.[8] When reaction was complete the crude product mixtures were successively oxidized, hydrolyzed (in the case of adducts of 6c), and methylated[9] (in the case of adducts of **6a** and **6c**) to give (eq 3) mixtures of **12** and **13** (overall yields from **6** are ca.



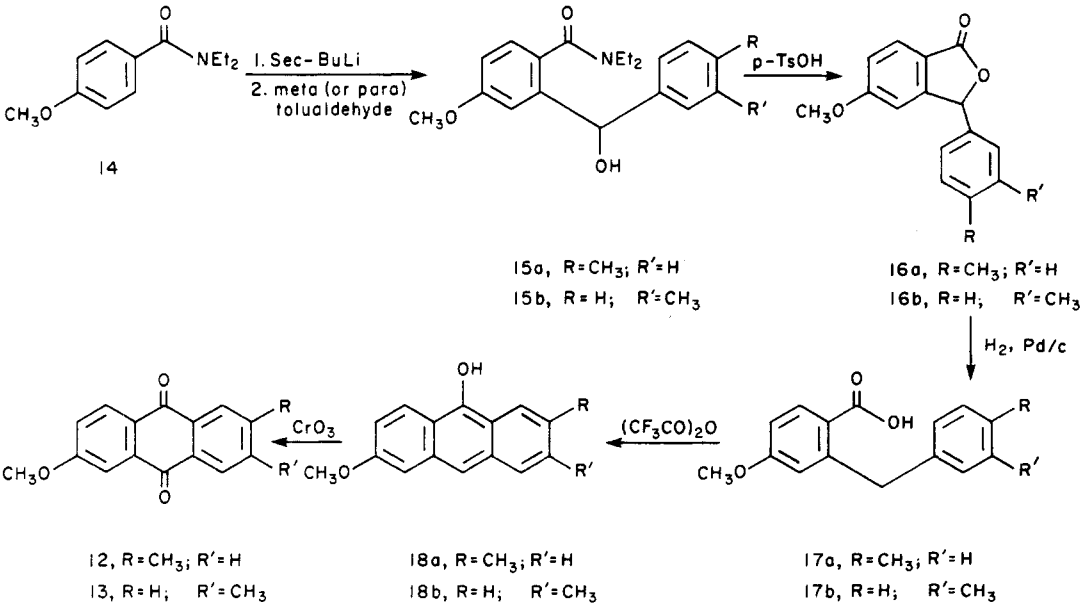
10, R = H; 12, R = CH_3 11, R = H; 13, R = CH_3 (3)

80%). All possible precautions (e.g., no recrystallizations) were taken to ensure that no adventitious enrichment of one isomer could occur and that the **12**/**13** ratio accurately reflected the **8**/**9** ratio. Authentic samples of **12** and **13** were secured by independent synthesis according to the method of Snieckus (Scheme I).[10]

Analysis of Mixtures of 12 and 13. The proton NMR spectra (at both 60 and 270 MHz) of **12** and **13** are so similar that ^1H NMR spectroscopy is not useful for determining the composition of mixtures of the two compounds. The two isomers **12** and **13** can be differentiated by ^{13}C NMR spectroscopy (see Experimental Section), but use of this method to analyze the mixtures of **12** and **13** was rejected when calibration studies using mixtures of **12** and **13** of varied, but known, composition indicated the absence of a good linear correlation between composition and relative peak heights for several pairs of resonances. Attempts to separate mixtures of **12** and **13** by TLC, analytical HPLC, and conventional gas chromatographic

(5) For an alternate explanation of regiochemistry see: Houk, K. N.; Tegmo-Larrson, I. M.; Rozeboom, M. D. *J. Org. Chem.* **1981**, *46*, 2338.
(6) For recent results consistent with this rationale see: Manning, W. B. *Tetrahedron Lett.* **1979**, 1661. Manning, W. B.; Muschik, G. M.; Tomaszewski, J. E. *J. Org. Chem.* **1979**, *44*, 699.
(7) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; p 152.
(8) Use of $CDCl_3$ as a solvent was precluded by the insolubility of **6a**.
(9) The methyl ethers **12** and **13** are substantially more soluble than the corresponding phenols.
(10) Snieckus, V.; de Silva, S. O. *Tetrahedron Lett.* **1978**, 5103.

Scheme I

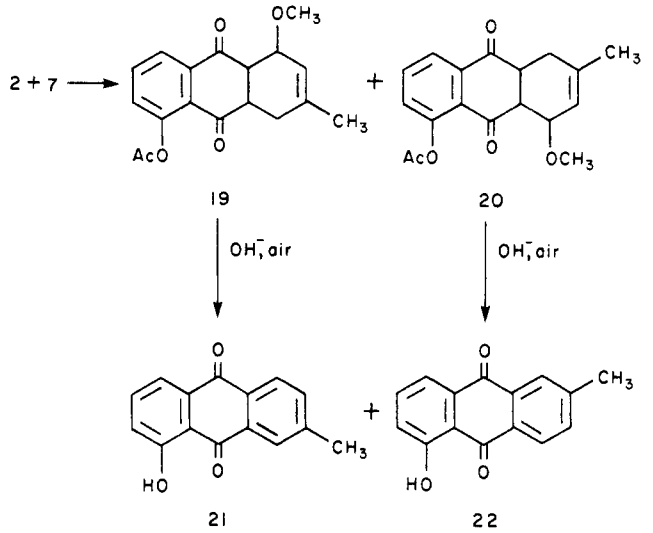


methods were completely unsuccessful. In contrast, gas chromatography employing nematic liquid crystals as the stationary/phase gave base-line resolution.[11,12] The ratios given in Table II were obtained by using this method.

Conclusion. The **8**/**9** ratios in Table II are in accord with the outcome predicted by invoking resonance donation from the C-6 substituent into the C-1 carbonyl.[2,3] Although the regioselectivity is attenuated in the case of **6c**, the acetoxy group nonetheless has an effect consistent with the hypothesis that it functions as a modest electron-donating substituent. While this finding is inconsistent with the Hammett σ constants for acetoxy (Table I), it is in agreement with the more refined analysis of Swain and Lupton[13] which attributes resonance donating properties to the acetoxy group.

It is perhaps noteworthy in this context that reaction of **2** with **7** also provides a 60:40 mixture of adducts **19** and **20**, respectively (Scheme II). It would thus appear that electronic factors predominate over peri or other effects which might be invoked to explain the results in eq 1.

Scheme II



Experimental Section

NMR spectra (60 MHz) were obtained with an Hitachi Perkin-Elmer Model R-24 instrument. A Varian FT-80A spectrometer was used to record the 80-MHz ^1H and ^{13}C NMR spectra. The 270-MHz spectra were obtained at the Francis Bitter National Magnet Laboratory at MIT. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane, and J values are given in hertz. Brinkmann Polygram Sil G/UV 254 plates (0.25 mm) were used for analytical TLC, and preparative separations were performed by using flash column chromatography on silica gel 60 (particle size 0.040–0.063 μm, EM reagents)[14] or 2-mm Analtech Uniplate silica gel GF plates. Melting points (Pyrex capillary) are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc.

The method of Teuber and Gotz[15] was used to prepare 6-hydroxy-1,4-naphthoquinone (**6a**) from 1,7-dihydroxynaphthalene. 6-Methoxy-1,4-naphthoquinone (**6b**) was prepared in almost quantitative yield according to the procedure of Garden and Thomson[16] except that the reaction was conducted in acetone at room temperature. Juglone acetate (**2**) was obtained by the method of Muxfeldt et al.[4a]

6-Acetoxy-1,4-naphthoquinone (6c). 6-Hydroxy-1,4-naphthoquinone (**6a**, 500 mg) was added to 5 mL of acetic anhydride and heated on a steam bath with intermittent shaking for 15 min. The resulting yellowish brown solution was cooled to room temperature and diluted with 50 mL of CH_2Cl_2. A saturated aqueous solution of $NaHCO_3$ (100 mL) was then added slowly (**Caution**: foaming) with stirring, the internal temperature being maintained below 40 °C. The mixture was stirred for 2 h, the CH_2Cl_2 layer separated, and the aqueous phase extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 layer and extracts were combined, washed with water and brine, dried (Na_2SO_4), and evaporated to give 470 mg (76%) of crude acetate **6c**.

The crude **6c** was dissolved in 20 mL of hot CH_3OH. The solution was cooled to 25 °C and filtered, and the insoluble material was washed with 10 mL of CH_3OH. The filtrate and wash were combined and concentrated to a volume of 15 mL, and 20 mL of H_2O was added. Most of the methanol was then removed on a rotary evaporator. The solid which had separated was collected by suction filtration, washed with water, and dried, giving

(11) (a) Janini, G. M.; Muschik, G. M.; Zielinski, W., Jr. *Anal. Chem.* **1976**, *48*, 809. (b) For recent applications see: Janini, G. M.; Manning, W. B.; Zielinski, W. L., Jr.; Muschik, G. M. *J. Chromatogr.* **1980**, *193*, 444. Manning, W. B. *Tetrahedron Lett.* **1981**, *22*, 1571.

(12) Separations were achieved at 230 °C on a 2.5% BBBT[11a] column. Retention times for **13** and **12** were 24 and 28.5 min, respectively.

(13) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

(14) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2933.

(15) Teuber, H. J.; Gotz, N. *Chem. Ber.* **1954**, *87*, 1236.

(16) Garden, J. F.; Thomson, R. H. *J. Chem. Soc.* **1957**, 2483.

264 mg (42%) of **6c**, mp 96–97 °C (lit.[17a] mp 102 °C). The NMR spectrum of **6c** is identical with that recently reported.[17b]

Diels–Alder Reaction of 6-Hydroxynaphthoquinone (6a) and *trans*-1-Methoxy-3-methyl-1,3-butadiene (7). 2-Hydroxy-6-methyl-9,10-anthraquinone (10) and 2-Hydroxy-7-methyl-9,10-anthraquinone (11). To a stirred solution of 500 mg (2.87 mmol) of **6a** in 6 mL of acetone-d_6 under N_2 was added 0.844 g (8.62 mmol, 3 equiv) of *trans*-1-methoxy-3-methyl-1,3-butadiene (**7**)[2b] at 25 °C. The reaction mixture was stirred until no **6a** remained as judged by NMR (~3.5 h). Volatile materials (including **7**) were then removed under vacuum (solvent was removed at aspirator vacuum on a rotary evaporator, and residual diene was removed at 1 mm) to give the crude gummy adduct mixture. This was dissolved in a mixture of 15 mL each of THF and absolute EtOH, and 30 mL of 2% NaOH(aq) was added (the solution turns blue). Oxygen was bubbled at room temperature through the reaction solution for 0.5 h. Acidification (to pH ~2) with 6 N HCl gave a precipitate which was collected, washed until the pH of the washes was ≥5, and dried to give 0.545 g (79.2%) of a mixture of **10** and **11** [the filtrate and wash were shown to contain negligible (<5 mg) amounts of **10** or **11**]. Without further purification the mixture of **10** and **11** was methylated directly as described below.

2-Methoxy-6-methyl-9,10-anthraquinone (12) and 2-Methoxy-7-methyl-9,10-anthraquinone (13). A portion (110 mg) of the **10**/**11** mixture was dissolved in 5 mL acetone under N_2. Silver(I) oxide (0.22 g) and 0.6 mL of CH_3I were added, and the mixture was stirred at 25 °C. After 1 and 2 h additional Ag_2O (2 × 110 mg) and CH_3I (2 × 0.3 mL) were added. Insoluble material was then removed by filtration and washed with acetone (50 mL). The combined filtrate and wash were concentrated in vacuo to give 115 mg (99%) of what was shown[12] to be a 3:1 mixture of **12** and **13**.

Diels–Alder Reaction of 6-Methoxynaphthoquinone (6b) and 7. To a stirred solution of 451 mg of **6b** in 5 mL of acetone-d_6 under N_2 was added 0.822 g (8.39 mmol, 3.5 equiv) of **7**[2b] at 25 °C. After 5 h the reaction was judged complete (NMR). Volatiles were removed under vacuum. The crude mixture of adducts was oxidized as above by dissolution in 15 mL each of THF and absolute EtOH, addition of 2% NaOH (25 mL), and exposure to oxygen. After 0.5 h the product was precipitated by acidification (to pH ~2) with 6 N HCl. Filtration followed by aqueous washing and drying as above gave 475 mg (79%) of a 3:1 mixture[12] of **12** and **13** (CH_2Cl_2 extraction of the filtrate and wash yielded <5 mg of **12**/**13**).

Diels–Alder Reaction of 6-Acetoxynaphthoquinone (6c) and 7. To a stirred solution of 200 mg (0.925 mmol) **6c** in 4 mL of acetone-d_6 under N_2 was added 3 equiv (0.27 g) of **7**[2b] at 25 °C. After 2 h the reaction was judged (NMR) complete, and volatiles were removed in vacuo. The residual mixture of adducts (NMR demonstrated that no acetate hydrolysis had occurred) was dissolved in a mixture of 7 mL each of THF and absolute EtOH, and 15 mL 2% NaOH was added (reaction mixture turns blue). Oxygen was bubbled through the stirred solution for 0.5 h. After a further 3 h at 25 °C an additional 10 mL of 2% NaOH was added, and the reaction mixture was heated to 50–55 °C for 10 min to ensure acetate hydrolysis. After the mixture cooled to room temperature, acidification and isolation as above gave 171.2 mg (78%) of a mixture of the anthraquinones **10** and **11**.

A portion (80 mg) of this mixture was methylated exactly as described for **10**/**11** obtained from **6a** and **7** to give 83.5 mg (99%) of a 60:40 mixture[12] of **12** and **13**.

Diels–Alder Reaction of Juglone Acetate (2) and 7. 1-Hydroxy-7-methyl-9,10-anthraquinone (21) and 1-Hydroxy-6-methyl-9,10-anthraquinone (22). To a stirred solution of 200 mg (0.925 mmol) of juglone acetate (**2**) in 5 mL of acetone-d_6 under N_2 was added 0.272 g (3 equiv) of **7** at 25 °C. After 4 h the reaction was judged (NMR) complete, and volatiles were removed in vacuo. The crude mixture of adducts was saponified, oxidized, and isolated as described for the adducts of **6a** and **6c** to give 180 mg (81%) of a mixture of **21** and **22** (extraction of the filtrate/aqueous wash gave negligible amounts of **21** and **22**). The composition of the mixture was shown to be approximately 60:40 (±5%) **21**/**22** by integration of the sharp OH singlets in the 270-MHz spectrum of the mixture.[18]

3-(4-Methylphenyl)-5-methoxyphthalide (16a). To a stirred solution of 5 g (24.2 mmol) of *N,N*-diethyl-*p*-anisamide (**14**)[19] in 40 mL of anhydrous ether under N_2 at −78 °C was added 19 mL (26.6 mmol) of 1.4 M *sec*-BuLi in hexane over 1 h. Neat *p*-tolualdehyde (2.9 g, 24.2 mmol) was then added in one portion. The reaction mixture was stirred at −78 °C for 10 min, the dry ice/acetone bath was then removed, and stirring was continued for an additional 4 h. Water (100 mL) was added, and the organic phase was separated, washed with water (4 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo to give 4.3 g of a thick syrup which contained the desired product (**15a**) as well as, inter alia, **14**, *p*-tolualdehyde, and **16a**. The *p*-tolualdehyde was removed by flash chromatography with 9:1 CH_2Cl_2/Et_2O followed by elution with acetone to give 1.9 g of a mixture predominating in **15a** but contaminated (NMR and TLC) with some **14** and **16a**. The **15a** so isolated was used in the next step without further purification.

A solution of crude hydroxyamide **15a** (1.0 g, crude mixture as obtained above) in 100 mL of toluene was refluxed with 580 mg of *p*-toluenesulfonic acid for 6 h. Removal of the toluene in vacuo gave a gummy reside which was chromatographed (flash column). Elution with 4:1 CH_2Cl_2/toluene gave 300 mg of **16a** (everything else remained on the column with this solvent system): mp 95 °C; ^1H NMR ($CDCl_3$) δ 2.3 (3 H, s), 3.82 (3 H, s), 6.3 (1 H, s), 6.7–7.2 (6 H, m), 7.85 (1 H, d, J = 6). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.54. Found: C, 75.44; H, 5.56.

4-Methoxy-2-[(4-methylphenyl)methyl]benzoic Acid (17a). A stirred mixture of 1.3 g of **16a** and 0.36 g of 5% Pd/C in 107 mL of glacial acetic acid was stirred under 1 atm of H_2 for 6 h at 80 °C. Filtration and removal of the acetic acid gave 1.0 g (76%) of acid **17a**: mp 130 °C; ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s), 3.85 (3 H, s), 4.49 (2 H, s), 6.75 (1 H, s), 7.15 (5 H, m), 8.25 (1 H, d, J = 6), 11.9 (1 H, s). Acid **17a** so obtained was sufficiently pure to use in the next reaction without further purification.

2-Methoxy-6-methyl-9,10-anthraquinone (12). To a stirred solution of 1.0 g (3.9 mmol) of acid **17a** in 33 mL of chloroform under N_2 at 25 °C was added 1.1 mL (7.8 mmol) of trifluoroacetic anhydride over 0.5 h. After an additional 3 h, solid Na_2CO_3 was added (to pH ~10) followed by 11 mL of 1:1 (v/v) H_2O/CH_3OH. The mixture was refluxed 2 h, cooled, and extracted with 50 mL of $CHCl_3$. The $CHCl_3$ extract was separated, washed (25 mL of H_2O, 25 mL of brine) and dried (Na_2SO_4). Removal of the solvent gave 0.93 g of a gummy solid. NMR and TLC analysis indicated that the gummy solid was a mixture of 2-methyl-6-methoxy-9-anthranol (**18a**, major component) and the corresponding anthraquinone (**12**, minor component).

To the above mixture (0.93 g) dissolved in 10 mL of glacial acetic acid was added a solution of 510 mg of CrO_3 in 16 mL of glacial acetic acid.[20] The reaction mixture was stirred 4 h at room temperature and diluted with 10 mL of water. The precipitate was collected, washed with water, and dried to give 730 mg of crude quinone **12** which was subjected to preparative thin-layer chromatography (1:1 CH_2Cl_2/pentane) to give 317 mg of pure **12** (32% overall yield). Recrystallization from Et_2O/EtOH (20:1) furnished an analytical sample: mp 192–193 °C (lit.,[21] mp 177 °C); ^1H NMR ($CDCl_3$, 80 MHz) δ 2.53 (3 H, s), 3.98 (3 H, s), 7.26 (1 H, dd, J = 8.6, 2.6), 7.56 (1 H, br d, J = 7.8), 7.72 (1 H, d, J = 2.6), 8.09 (1 H, br s), 8.18 (1 H, d, J = 7.9), 8.25 (1 H, d, J = 8.7). ^{13}C NMR ($CDCl_3$) δ 182.85, 182.26, 164.22, 145.13, 135.65, 134.26, 133.51, 131.31, 129.53, 127.23, 120.74, 109.87, 55.77, 21.74. Two resonances are apparently superimposed. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.27; H, 4.83.

3-(3-Methylphenyl)-5-methoxyphthalide (16b). By use of a procedure (including chromatography) analogous to that employed for the preparation of **15a**, 13.2 g of a mixture rich in

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hydroxy amide **15b** was obtained from 25 g of **14**, 133 mmol of *sec*-BuLi (hexane), and 14.5 g of *m*-tolualdehyde.

Treatment of a similar mixture (13.2 g) with 7.9 g of *p*-toluenesulfonic acid in toluene as in the case of **15a** gave, after purification, 3.19 g of **16b**: mp 90 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s), 3.9 (3 H, s), 6.40 (1 H, s), 6.8 (1 H, br s), 7.15–7.35 (5 H, m), 8.05 (1 H, d, J = 6). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.54. Found: C, 75.61; H, 5.61.

4-Methoxy-2-[(3-methylphenyl)methyl]benzoic Acid (17b). Hydrogenolysis of 1.0 g of **16b** by using the procedure for the conversion of **16a** to **17a** gave acid **17b**: mp 85–86 °C; 99% yield; ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s), 3.85 (3 H, s), 4.45 (2 H, s), 6.75 (1 H, s), 6.9–7.25 (5 H, m), 8.15 (1 H, d, J = 9), 9.15 (1 H, br s). Acid **17b** so obtained was sufficiently pure to use directly in the next reaction.

2-Methoxy-7-methyl-9,10-anthraquinone (13). Conversion of **17b** to **13** via anthranol **18b** was effected by a procedure identical with that used for the preparation of **12** from **17a**. Anthraquinone **13** (mp 162–163 °C) was obtained in 39% overall yield from acid **17b**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.52 (3 H, s), 3.98 (3 H, s), 7.24 (1 H, dd, J = 8.3, 2.8), 7.58 (1 H, br d, J = 8), 7.72 (1 H, d, J = 2.5), 8.08 (1 H, br s), 8.19 (1 H, d, J = 8), 8.25 (1 H, d, J = 8.5). ^{13}C NMR ($CDCl_3$) δ 183.31, 181.84, 164.12, 144.54, 135.58, 134.77, 133.43, 131.38, 129.50, 127.28, 127.21, 120.86, 109.88, 55.98, 21.67. Two resonances are apparently superimposed. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.01; H, 4.87.

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Registry No. **2**, 5196-28-1; **6a**, 4923-53-9; **6b**, 29263-68-1; **6c**, 71186-88-4; **7**, 73451-87-3; **10**, 83312-50-9; **11**, 83312-51-0; **12**, 83312-52-1; **13**, 83333-48-6; **14**, 7465-86-3; **15a**, 83312-53-2; **16a**, 83312-54-3; **16b**, 83312-56-5; **17a**, 83312-55-4; **17b**, 83312-57-6; **21**, 68963-23-5; **22**, 68963-22-4.

Notes

Conformation of 1,2-Adducts of *N*-Halo Amides and *tert*-Butylethylene by High-Field Proton Nuclear Magnetic Resonance Spectroscopy

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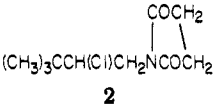
Conformational preference and potential barriers for rotation about single bonds in open-chain fragments is a field of continued interest.[2,3] We report herein the ^{1}H NMR data at 400 MHz of *N*-(2-halo-3,3-dimethylbutyl) amides **1** and *N*-(2-chloro-3,3-dimethylbutyl)succinimide

$(CH_3)_3CCH(X)CH_2NHCOZ$

1a, X = Cl; Z = CH_3
b, X = Cl; Z = CH_2Cl
c, X = Cl; Z = CCl_3
d, X = Cl; Z = CF_3
e, X = Cl; Z = OCH_2CH_3
f, X = Br; Z = CCl_3



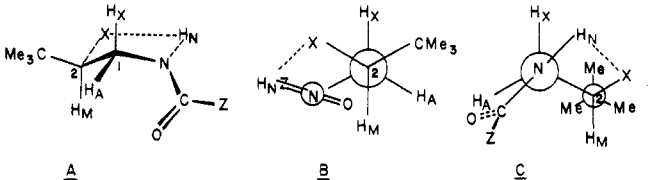
2

(**2**) which show a strong preference for one conformation about the C_1–C_2 and C_1–N single bonds in $CDCl_3$.

Compounds **1** were obtained by the photochemical addition of *N*-halo amides (ZCONHX) to *tert*-butylethylene in the course of a study of the influence of Z on the quantum yield of the reaction.[4] The preparation of **2** by the photochemical addition of *N*-chlorosuccinimide to *tert*-butylethylene has been reported.[5]

Table I lists the ^{1}H NMR data for compounds **1** at ca. 27 °C. The two methylenic protons at C-1 (H_A and H_X) and the halomethine proton at C-2 (H_M) form an AMX system. The methylenic protons are further coupled with the proton on nitrogen (H_N), and each of them appears as a doublet of doublets of doublets which becomes a double doublet upon irradiating the NH. The large chemical shift difference between the two methylenic protons is noteworthy (from 0.8 ppm in **1f** to 1.2 ppm in **1a**): proton H_A absorbs at a lower field and proton H_X at a higher field than the halomethine proton H_M. The attribution of the coupling constants was confirmed by spin-decoupling experiments: $J_{AX} = J_{gem}$ = 14.0–14.2 Hz; J_{AM} = 2.4–2.6 Hz; J_{MX} = 10.5–10.7 Hz; J_{AN} = 7.8–8.3 Hz; J_{XN} = 3.5–3.9 Hz. All the protons of the bromo derivative **1f** are more deshielded than the corresponding protons of the chloro analogue **1c**: H_N by 0.13 ppm, H_A by 0.04 ppm, H_M by 0.11 ppm, H_X by 0.16 ppm, and the *tert*-butyl group by 0.15 ppm.

The preferred conformation of compounds **1** is shown in the three-dimensional formula A[6] and the corresponding



A B C

Newman projections B (along the C_1–C_2 bond), and C (along the N–C_1 bond). This conformation follows from

(1) NATO Visiting Scientist (1980–1981) from the Faculté des Sciences, Besançon, France.

(2) Inter alia, see the following reviews and references therein: (a) Zefirov, N. S. *Tetrahedron* **1977**, *33*, 3193. (b) Ōki, M. *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 87. (c) Sternhell, S. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds; Academic Press: New York, 1975. (d) Dale, *J. Tetrahedron* **1974**, *30*, 1683. (e) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

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