5.57 (d, 1 H, H-7) (J = 4 Hz), 5.91 (dd, 1 H, H-14) (J = 11, 11 Hz); MS (EI) m/z (relative intensity) 583 (M^+, 6.3), 146 (40), 100 (100). Anal. Calcd for $C_{28}H_{43}NO_9$: C, 62.55; H, 8.06; N, 2.61. Found: C, 62.07; H, 8.05, N, 2.49.

1-(Morpholinoacetyl)forskolin (5). To a stirred solution of 2.0 g (4.88 mmol) of **1a** in 20 mL of dichloromethane was added 0.75 g (6.20 mmol) of dimethylaniline. The solution was cooled in an ice bath and a solution of 0.47 mL (1.09 g, 5.40 mmol) of bromoacetyl bromide in 20 mL of dichloromethane was added dropwise. The resulting blue solution was stirred in an ice bath for 1 h and poured into ice/dichloromethane/sodium bicarbonate, and the organic layer was separated, washed with water and brine, dried (Na_2SO_4), and concentrated to an oil.

The oil was dissolved in 20 mL of dichloromethane and added dropwise to a solution of 3 mL of morpholine in 20 mL of ethyl acetate in an ice bath. Following the addition the solution was stirred for 1 h in an ice bath and worked up as above to provide an oil. The oil was flash chromatographed on silica gel (eluent 25%, 50% ethyl acetate/hexanes) to provide **5** (2.12 g, 80.7%). Recrystallization from cyclohexane/ethyl acetate provided material that was identical by mp, IR, NMR, and MS with that prepared from **2**. Anal. Calcd for $C_{28}H_{43}NO_9$: C, 62.55; H, 8.06; N, 2.61. Found: C, 62.73; H, 8.14; N, 2.60.

Forskolin-1,9-Dimethylformamide Acetal (6). Forskolin (**1a**) (100 mg, 0.244 mmol) was dissolved in 1 mL of DMF dimethyl acetal and stirred for 20 h at 55 °C. The mixture was dissolved in ether, washed with water, dried (Na_2SO_4), filtered, and concentrated to an oil. The material was purified by flash chromatography on silica gel (eluent 3% methanol/dichloromethane) to provide **6** as an oil (85 mg, 79.1%): IR ($CHCl_3$) 2960, 1738, 1712, 1118, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 2.16 (s, 3 H, $COCH_3$), 2.28 (d, 1 H, H-5) (J = 2 Hz), 2.37–2.48 (d, 7 H, H-12, $N(CH_3)_2$), 2.87 (d, 1 H, H-12) (J = 16 Hz), 4.14 (m, 1 H, H-1), 4.49 (m, 1 H, H-6), 4.76 (s, 1 H, OCHN), 4.97 (dd, 1 H, H-15) (J = 11 Hz), 5.34 (dd, 1 H, H-15) (J = 17 Hz), 5.22 (d, 1 H, H-7) (J = 4 Hz), 5.82 (dd, 1 H, H-14) (J = 11, 10 Hz); MS (CI) m/z (relative intensity) 466 (M^+ + 1, 23), 421 (100), 315 (53). Anal. Calcd for $C_{25}H_{39}NO_7$: C, 64.49; H, 8.44; N, 3.01. Found: C, 64.69; H, 8.25; N, 3.09.

7-Desacetylforskolin-1,9-Dimethylformamide Acetal (7) (from 1a). A solution of 100 g (0.244 mol) of **1a** in 400 mL of DMF dimethyl acetal was stirred at 60–70 °C for 20 h. The solution was concentrated in vacuo and the residue dissolved in 400 mL of methanol to which was added a solution of 2 L of methanol and 600 mL of saturated potassium carbonate. The resulting mixture was stirred at 50–55 °C for 2 h after which was added 1.2 L of water. The mixture was allowed to stand overnight, filtered, and washed with methanol/water to provide **7** (76.6 g, 74.2%). The material was recrystallized from cyclohexane to provide colorless prisims, mp 144–147 °C: IR ($CHCl_3$) 2970, 1742, 1718, 1223, 1122 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05, (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 2.18–2.48 (m, 8 H, H-5, H-12, $N(CH_3)_2$), 2.88 (d, 1 H, H-12) (J = 16 Hz), 4.03 (d, 1 H, H-7) (J = 4 Hz), 4.13 (m, 1 H, H-1), 4.51 (m, 1 H, H-6), 4.74 (s, 1 H, OCHN), 4.98 (d, 1 H, H-15) (J = 11 Hz), 5.22 (d, 1 H, H-15) (J = 17 Hz), 5.97 (dd, 1 H, H-14) (J = 11, 10 Hz); MS (CI) m/z (relative intensity) 424 (M^+ + 1, 6.1), 423 (M^+, 35), 378 (100), 333 (61), 263 (54). Anal. Calcd for $C_{23}H_{37}NO_6$: C, 65.22; H, 8.81; N, 3.31. Found: C, 65.18; H, 8.76; N, 3.25.

7-Desacetyl-7-(morpholinoacetyl)forskolin-1,9-Dimethylformamide Acetal (8). To a stirred solution of 2.0 g (4.73 mmol) of **7**, 1.03 g (5.67 mmol) of morpholinoacetic acid hydrochloride, 1.15 g, (9.43 mmol) of DMAP, and 20 mL of dichloromethane was added 1.17 g (5.68 mmol) of DCC. The mixture was stirred for 20 h at room temperature after which an additional 1.17 g (5.68 mmol) of DCC and 1.15 g (9.43 mmol) of DMAP were added. The suspension was stirred for an additional 5 h after which were added 0.75 g of morpholinoacetic acid hydrochloride and 0.5 g (4.10 mmol) of DMAP. After being stirred for 20 h at room temperature, the suspension was filtered, diluted with dichloromethane, washed twice with sodium bicarbonate and once with water, dried (Na_2SO_4), filtered, and concentrated to an oil. The oil was purified by flash chromatography on silica gel (eluent 20% acetone/hexanes) to provide **8** (1.28 g, 49.3%), which crystallized on standing: mp 178–188 °C; IR ($CHCl_3$) 3023, 1756, 1723, 1122 cm^{-1}; ^1H NMR ($CHCl_3$) δ 1.02 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 2.27 (d, 1 H, H-5) (J = 2 Hz), 2.35–2.45 (m, 7 H, H-12, $N(CH_3)_2$), 2.64 (m, 4 H, CH_2NCH_2), 2.86 (d, 1 H, H-12) (J = 16 Hz), 3.31 (s, 2 H, $COCH_2N$), 3.75 (m, 4 H, CH_2OCH_2), 4.11 (br s, 1 H, H-1), 4.48 (br s, 1 H, H-6), 4.74 (s, 1 H, OCHN), 4.94 (dd, 1 H, H-14) (J = 10 Hz), 5.28 (d, 1 H, H-14) (J = 18 Hz), 5.45 (d, 1 H, H-7) (J = 4 Hz), 5.80 (dd, 1 H, H-15) (J = 10, 10 Hz); MS (CI) m/z (relative intensity) 551 (M^+ + 1, 1.1), 506 (100), 284 (40). Anal. Calcd for $C_{29}H_{26}N_2O_8$: C, 63.25; H, 8.42; N, 5.09. Found: C, 63.28; H, 8.37; N, 5.01.

7-Desacetyl-7-(morpholinoacetyl)forskolin (3). A solution of 300 mg (0.544 mmol) of **8** in 6 mL of methanol and 6 mL of 80% aqueous acetic acid was stirred for 48 h at room temperature. The solution was poured into ice/ethyl acetate/water, and the organic layer separated, washed twice with water and once with brine, dried (Na_2SO_4), filtered, and concentrated to an oil. The material was flash chromatographed on silica gel (eluent 20%, 30% ethyl acetate/hexanes) to provide **3** (0.173 g, 64.2%). Recrystallization from hexane/ethyl acetate provided analytically pure material identical by mp, IR, NMR, and MS with the compound prepared from esterification of **1b** with DCC, DMAP, and morpholinoacetic acid (see above). Anal. Calcd for $C_{26}H_{41}NO_8$: C, 63.01; H, 8.34; N, 2.83. Found: C, 63.16; H, 8.36; N, 2.67.

7-Desacetyl-6-(morpholinoacetyl)forskolin (9). To a stirred solution of 200 mg (0.404 mmol) of **3** in 4 mL of dry THF in an ice bath was added 0.41 mL of a 1 M solution of lithium bis(trimethylsilyl)amide in THF. The solution was stirred at 0–5 °C for 1 h and allowed to warm to room temperature, after which it was poured into ice/water, extracted with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated to an oil. The oil was purifed by flash chromatography on silica gel (eluent 40, 50, 60% ethyl acetate/hexanes) and the product-containing fractions were combined and concentrated to provide **9** (61 mg, 30.5%). Recrystallization from ethyl acetate provided analytically pure material: mp 199–204 °C; IR ($CHCl_3$) 3023, 1748, 1720, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 2.36 (d, 1 H, H-5) ($J_{6,5}$ = 2 Hz), 2.53 (d, 1 H, H-12) (J = 17 Hz), 2.54 (m, 4 H, CH_2NCH_2), 3.19 (s, 2 H, $COCH_2N$), 3.21 (d, 1 H, H-12) (J = 17 Hz), 3.74 (m, 4 H, CH_2OCH_2), 4.30 (d, 1 H, H-7) (J = 4 Hz), 4.66 (m, 1 H, H-1), 5.00 (d, 1 H, H-15) (J = 11 Hz), 5.19 (d, 1 H, H-15) (J = 17 Hz), 5.93 (m, 1 H, H-6), 6.12 (d, 1 H, H-14) (J = 11, 11 Hz); MS (CI) m/z (relative intensity) 496 (M^+ + 1, 100), 478 (28), 146 (29). Anal. Calcd for $C_{26}H_{41}NO_8$: C, 63.01; H, 8.34; N, 2.83. Found: C, 63.29; H, 8.61; N, 3.11.

Acknowledgment. We thank Anastasia Linville, Dana Hallberg, and Marc Agnew for spectra data and Drs. Helen H. Ong, Richard C. Allen, Nicholas J. Hrib, and Gregory M. Shutske for helpful discussions.

Registry No. **1a**, 66575-29-9; **1a** (1-bromoacetate), 120385-34-4; **1b**, 64657-20-1; **1b** (1-bromoacetate), 120385-33-3; **2**, 120385-29-7; **3**, 108211-64-9; **4**, 120385-30-0; **5**, 120385-31-1; **6**, 105575-66-4; **7**, 105535-42-0; **8**, 120385-32-2; **9**, 111124-64-2; $(CH_3)_2NCH(OCH_3)_2$, 4637-24-5.

π-Facial Selectivity in Norbornenobenzoquinone–Tropone Cycloaddition

Goverdhan Mehta* and Srinivasa Rao Karra

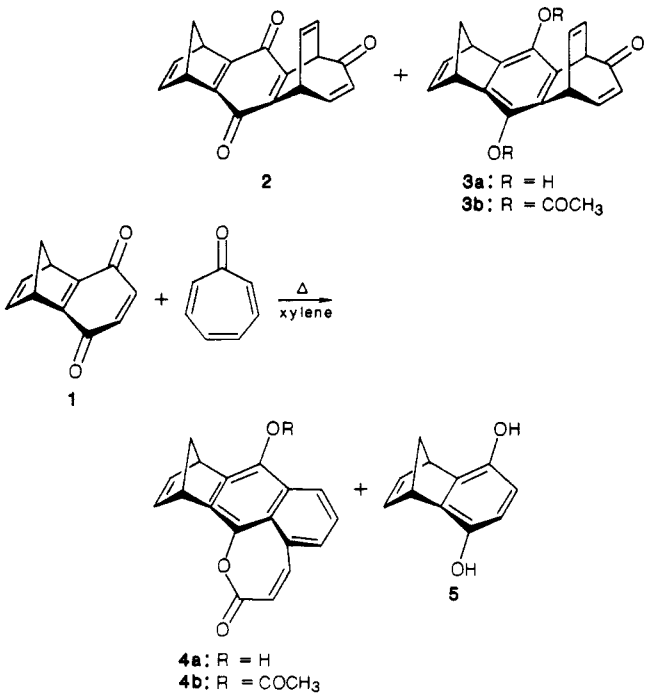
School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

Received December 15, 1988

During the recent past, cycloaddition chemistry of tropone has been extensively investigated from mechanistic as well as synthetic perspectives.[1] Tropone has been

0022-3263/89/1954-2975$01.50/0

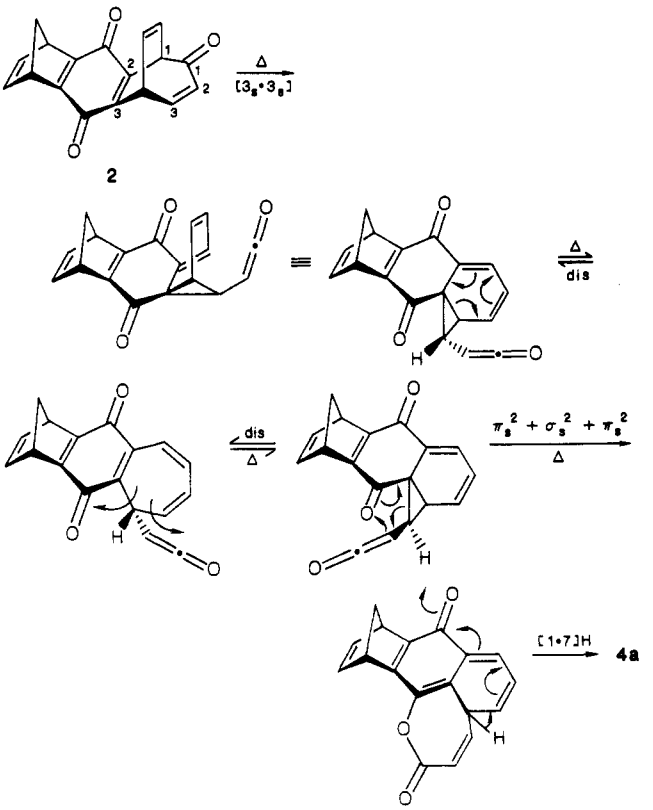
Scheme I



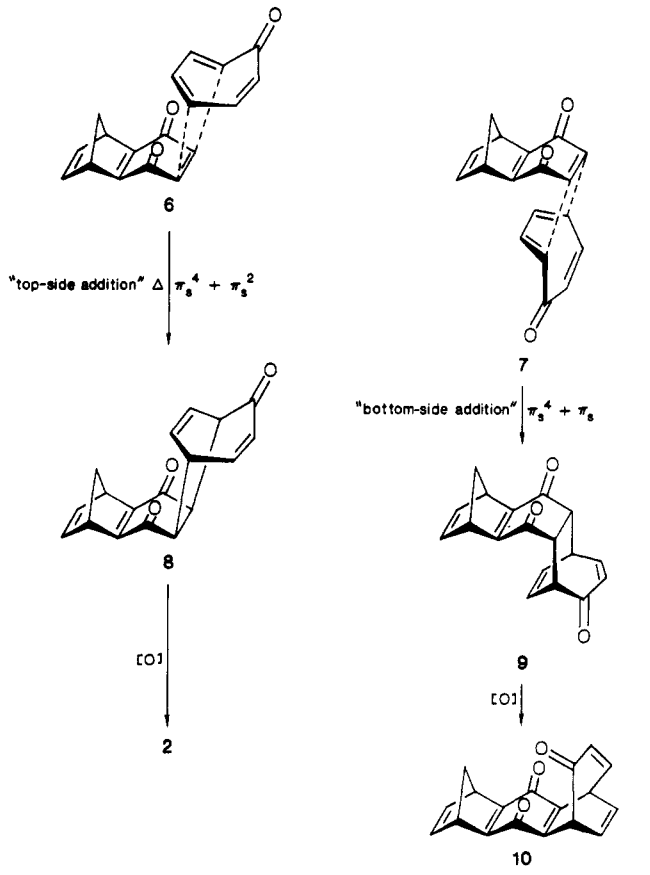
recognized as a versatile cycloaddend and can function as a 2π, 4π, or 6π component in the cycloaddition processes. In particular, Diels–Alder adducts of tropone with a wide variety of dienophiles have been reported, and the resulting bicyclo[3.2.2]nonadienones, in turn, have interesting and synthetically exploitable chemistry.[2] However, tropone has been reported to be inert toward the dienophile benzoquinone, and their 4 + 2 cycloaddition product remains unknown.[3] In this note, we describe the *first* example of cycloaddition of tropone to an unactivated benzoquinone derivative.[4]

Heating norbornenobenzoquinone (1) with tropone in refluxing xylene followed by column chromatography resulted in the isolation of three 1:1 products, **2**, **3a** and **4a**, in a ratio of 1:6:2, along with a considerable amount of the reduced product **5** (Scheme I). The structures of **2** and **3a** were established through the presence of α,β-unsaturated carbonyl group in their IR spectra, the presence of diagnostic resonances due to six olefinic protons in the ^1H NMR spectra and the quinol–quinone redox relationship

Scheme II



Scheme III



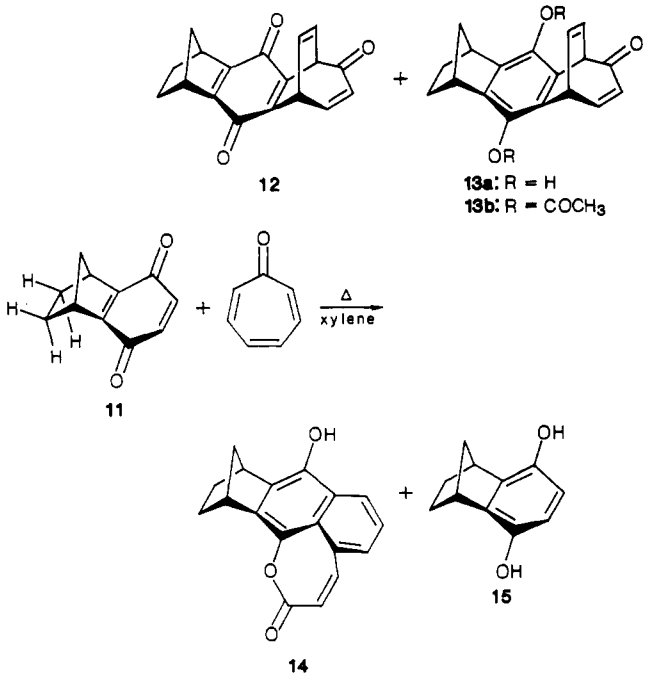
(1) (a) Cookson, R. C.; Drake, B. V.; Hudec, J.; Morrison, A. *J. Chem. Soc., Chem. Commun.* **1966**, 15. (b) Ito, S.; Fujise, Y.; Woods, M. C. *Tetrahedron Lett.* **1967**, 1059. (c) Ito, S.; Takeshita, H.; Shoji, Y.; Toyooka, Y.; Nozoe, T. *Ibid.* **1968**, 3215. (d) Ito, S.; Takeshita, H.; Shoji, Y. *Ibid.* **1969**, 1815. (e) Ciabattoni, J.; Gowley, J. F.; Kende, A. S. *J. Am. Chem. Soc.* **1967**, *89*, 2778. (f) Kinstle, T. H.; Carpenter, P. D. *Tetrahedron Lett.* **1969**, 3943. (g) Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4145. (h) Mukai, T.; Akasaki, Y.; Hagiwarsa, T. *Ibid.* **1972**, *94*, 675. (i) Sasaki, T.; Kanematsu, K.; Hayakawa, K. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1951. (j) Tanida, T.; Pfaendler, H. R. *Helv. Chim. Acta* **1972**, *55*, 3062. (k) Ito, S.; Ohtani, H.; Narita, S.; Honma, H. *Tetrahedron Lett.* **1972**, 2223. (l) Paddon Row, M. N.; Warrener, R. N. *Ibid.* **1974**, 3797. (m) Takeshita, H.; Wada, Y.; Mori, A.; Hatsui, T. *Chem. Lett.* **1973**, 335. (n) Jones, D. W.; Kneen, G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1647. (o) Sasaki, T.; Kanematsu, K.; Lizuka, R. *J. Org. Chem.* **1976**, *41*, 1105. (p) Garst, M. E.; Roberts, V. A.; Prussin, C. *Tetrahedron* **1978**, *39*, 581. (q) Mukerjee, D.; Watts, C. R.; Houk, K. N. *J. Org. Chem.* **1983**, *43*, 4170. (r) Garst, M. E.; Roberts, V. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 3882. (s) Paquette, L. A.; Hathaway, S. J.; Schirch, P. F. T. *J. Org. Chem.* **1985**, *50*, 4199. (t) Tian, G. R.; Sugiyama, S.; Mori, A.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2393. (u) Rigby, J.; Moore, T.; Rege, S. *J. Org. Chem.* **1986**, *51*, 2398. (v) Funk, R.; Bolton, G. *J. Am. Chem. Soc.* **1986**, *108*, 4665.

(2) (a) Uyehara, T.; Ogata, K.; Yamada, J.; Kato, T. *J. Chem. Soc., Chem. Commun.* **1983**, 17. (b) Uyehara, T.; Yamada, J.; Kato, T.; Bohlmann, F. *Tetrahedron Lett.* **1983**, 4445. (c) Uyehara, T.; Yamada, J.; Kato, T. *Tetrahedron Lett.* **1985**, 5069. (d) Uyehara, T.; Kabasawa, Y.; Kato, T.; Furuta, T. *Ibid.* **1985**, 2347. (e) Uyehara, T.; Furuta, T.; Kabasawa, Y.; Yamada, J.; Kato, T. *Ibid.* **1986**, 539.

(3) Kanematsu, K.; Morita, S.; Fukushima, S.; Osawa, E. *J. Am. Chem. Soc.* **1981**, *103*, 5211.

(4) (a) Diels, O.; Alder, K. *Ber. Itsch. Chem. Ges.* **1929**, *62*, 2337. (b) Meinwald, J.; Wiley, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 3667. (c) Cookson, R. C.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3043.

Scheme IV



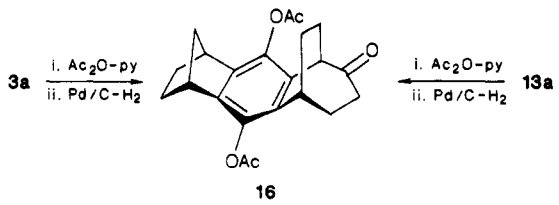
between them revealed through the facile oxidation of **3a** to **2** by Ag_2O. The mass spectrum of **2** (m/z 276, M^+) clearly showed that it was derived from the dehydrogenation of the initially formed 1:1 Diels–Alder adduct between **1** and tropone. Further evidence in support of formulation **2** is presented later in the sequel. The substantial intervention of redox processes during the cycloaddition reaction was supported by isolation of a considerable amount of **5** derived from **1** during the reaction.

The unusual ϵ-lactone structure of **4a** was established on the basis of complimentary spectral data and the observation that on heating **2** was swiftly converted to **4a** in high yield. The diagnostic features of the ^1H NMR spectrum of **4a** were the presence of a highly deshielded proton resonance at δ 8.12 (dd) due to the *peri*-hydrogen of a α-naphthol moiety and two olefinic protons at δ 7.0 (d, J = 12 Hz) and δ 6.02 (d, J = 12 Hz) as part of AB quartet typical of the C=CC(=O)O type structural fragment. The latter signals disappeared when **4a** was partially hydrogenated over 10% Pd/C catalyst. In conformity with formulation **4a**, the monoacetate **4b** exhibited an 18-line ^{13}C NMR spectrum having 14 sp^2 carbon signals. Formation of **4a** can be rationalized via **2** through a series of pericyclic reactions indicated in Scheme II. There is a precedence for the formation of a ketene intermediate during the thermolysis of bicyclo[3.2.2]nonadienones.[1f,t]

The 4 + 2 addition of tropone to **1** can be visualized as proceeding through either of the two endo modes **6** or **7** leading to adducts **8** and **9**, respectively (Scheme III). Since the initially formed 4 + 2 adduct of **1** and tropone suffers dehydrogenation during the reaction conditions (vide supra), the resulting product could be either **2** or **10**, depending upon the facial selectivity during the cycloaddition process (Scheme III). The question of facial selectivity and therefore of the resulting product structure **2** or **10** was resolved as follows.

It is known through Cookson's[4c] and our work[5,6] that norbornanobenzoquinone **11** (dihydro-**1**) exhibits facial

Scheme V



selectivity in cycloaddition reactions in favor of "top-side" addition due to the increased steric hindrance of the ethano bridge from "bottom side". We therefore studied the cycloaddition of tropone with **11**.[4c] Once again three 1:1 adducts, **12**, **13a**, and **14**, were isolated (4:12:1 ratio) along with the quinol **15** (Scheme IV). Structures to these adducts were assigned on the basis of spectral characteristics summarized in the Experimental Section. The 1:1 adducts **3a** and **13a** obtained from **1** and **11**, respectively, were now correlated as shown in Scheme V to furnish the same saturated diacetate **16**. This established the stereostructure of the adducts **2** and **3a**, which are formed through exclusive "top-side" addition shown in **6**.

In summary, we have observed the 4 + 2 cycloadditions between a novel benzoquinone derivative **1** and tropone. The reaction is notable for the π-facial selectivity exhibited by the dienophile and the observation of an interesting rearrangement leading to the lactone **4a**. We are further investigating the π-facial selectivity exhibited by **1** in its cycloaddition chemistry.[6]

Experimental Section[7]

Reaction between 1,4-Dihydro-1,4-methanonaphthalene-5,8-dione (1) and Tropone. A mixture of norbornenobenzoquinone (**1**)[5] (500 mg, 2.906 mmol) and tropone[8] (365 mg, 3.44 mmol) in 15 mL of xylene was refluxed at 140 °C for 28 h under a nitrogen atmosphere. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel (20 g) column. After a forerun of the unreacted quinone **1** (200 mg), elution of the column with 20% ethyl acetate–hexane mixture gave **2** (30 mg, 9.8%), **4a** (55 mg, 18.0%), **3a** (173 mg, 56.9%), and quinol **5** (115 mg, mp 140 °C). Yields of **2**, **4a**, and **3a** are reported on the basis of the quinone **1** consumed. Quinone **2** was recrystallized from a dichloromethane–hexane mixture to furnish yellow crystals: mp 177 °C; IR (KBr) 1685, 1655, 1600, 1320, 620 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.2–6.96 (m, 1 H), 6.94–6.72 (m, 3 H), 6.64–6.4 (m, 1 H), 5.32–5.10 (m, 1 H), 5.04–4.88 (m, 1 H), 4.68–4.44 (br t, 1 H), 4.08 (br s, 2 H), 2.2–2.12 (m, 2 H); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 186.3, 180.7, 160.8, 160.4, 151.0, 142.7, 142.5, 142.4, 138.2, 129.8, 125.8, 74.0, 55.3, 48.4, 37.0; mass spectrum, m/z 276.0 (M^+). Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 77.98; H, 4.35. The lactone **4a** was also recrystallized from dichloromethane–hexane to furnish red crystals: mp 197 °C; IR (KBr) 3240, 1665, 1640, 1210, 820 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 8.12 (dd, J_1 = 6 Hz, J_2 = 4 Hz, 1 H), 7.40–7.20 (m, 2 H), 7.0 (d, $^1/_2$ AB, J = 12 Hz, 1 H), 6.76 (dd, $J_1 = J_2$ = 2 Hz, 2 H), 6.02 (d, $^1/_2$ AB, J = 12 Hz, 1 H), 5.20 (br s, 1 H), 4.42 (br s, 1 H), 4.12 (br s, 1 H), 2.36–2.10 (m, 2 H); mass spectrum, m/z 276.0 (M^+). Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.35; H, 4.37. Compound **3a** was recrystallized from ethyl acetate: mp 247 °C; IR (KBr) 3320, 1650, 1620, 1470 cm^{-1}; mass spectrum, m/z 278 (M^+). This compound was best characterized as its diacetate **3b** because of its highly insoluble nature (vide infra).

Thermolysis of the Quinone 2. The adduct quinone **2** (10 mg, 0.036 mmol) was dissolved in xylene and refluxed for 10 h. The solvent was removed, and the residue was filtered through a silica gel (1 g) column to furnish the lactone **4a** (8 mg, 80%). The product was recrystallized from a dichloromethane–hexane

(5) Mehta, G.; Padma, S. *J. Am. Chem. Soc.* **1987**, *109*, 7230.
(6) (a) Mehta, G.; Raja Reddy, K. *Tetrahedron Lett.* **1988**, 5309. (b) Mehta, G.; Padma, S.; Karra, S. R.; Gopidas, K. R.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1989**, *54*, 1342–1346; unpublished results.
(7) For a general write up on the Experimental Section, see: Mehta, G.; Rao, K. S. *J. Org. Chem.* **1985**, *50*, 5537.
(8) Prepared according to the procedure of Radlick, P. *J. Org. Chem.* **1964**, *29*, 960.

mixture, mp 197 °C, to give a product identical with that obtained above.

Silver(I) Oxide Oxidation of 3a to 2. The compound **3a** (10 mg, 0.036 mmol) was dissolved in ethyl acetate (3 mL) and stirred vigorously with silver(I) oxide (10 mg) in the presence of anhydrous Na_2SO_4 (10 mg) at room temperature. The reaction mixture turned yellow immediately, and after 15 min of stirring it was filtered. Removal of the solvent from the filterate under vacuum gave the crude quinone **2**, which was recrystallized from a dichloromethane–hexane mixture to furnish **2** (10 mg, 100%), identical with that obtained above.

Acetylation of 3a. The compound **3a** (100 mg, 0.36 mmol) was treated with a mixture of dry pyridine (0.5 mL) and acetic anhydride (2 mL). The reaction mixture was stirred at ambient temperature for 10 h and then poured into cold water (10 mL). The aqueous layer was extracted thoroughly with ether (3 × 20 mL), and the combined ethereal layer was washed with 10% HCl (10 mL), water (10 mL), and finally with brine (15 mL). Drying over anhydrous Na_2SO_4, removal of solvent, and recrystallization of the crude product from dichloromethane–hexane mixture gave the white crystalline pure diacetate **3b** (121 mg, 98%): mp 245 °C; IR (KBr) 1750, 1640, 1165, 880 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.20–7.0 (m, 1 H), 6.76 (br s, 3 H), 6.64–6.40 (m, 1 H), 5.20 (dd, $J_1 = J_2 = 4$ Hz, 1 H), 4.76–4.56 (m, 1 H), 4.26 (br t, 1 H), 3.8 (br s, 2 H), 2.40 (s, 6 H), 2.20 (br s, 2 H). Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.90; H, 5.01. Found: C, 72.86; H, 4.98.

Hydrogenation of the Diacetate 3b. The diacetate **3b** (17 mg, 0.049 mmol) was dissolved in ethyl acetate and hydrogenated over 10% palladium–carbon for 1 h. The catalyst was filtered, and the solvent was removed under vacuum. The crude product was recrystallized from a dichloromethane–hexane mixture to furnish the hydrogenated product **16** (17 mg, 94%): mp 195 °C; IR (KBr) 1750, 1700, 1180, 880 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 3.68–3.48 (m, 1 H), 3.32 (br s, 3 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 2.0–1.16 (m, 14 H). Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.71; H, 6.56. Found: C, 71.84; H, 6.60.

Acetylation of the Lactone 4a. The lactone **4a** (100 mg, 0.36 mmol) was dissolved in dry pyridine (0.5 mL) and acetic anhydride (2 mL) and left aside overnight. The reaction mixture was poured into cold water (15 mL), and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with 10% HCl (10 mL), water (10 mL), and finally with brine (15 mL). The ether extract was dried over anhydrous Na_2SO_4, and solvent was removed to give the crude acetate. It was recrystallized from a dichloromethane–hexane mixture to obtain the yellow crystalline acetate **4b** (113 mg, 99%): mp 155 °C; IR (KBr) 1745, 1700, 1180, 820 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.72 (dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, 1 H), 7.4–7.2 (m, 2 H), 7.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 6.8 (dd, $J_1 = J_2 = 2$ Hz, 2 H), 6.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 4.45 (br s, 1 H), 3.94 (br s, 1 H), 2.48 (s, 3 H), 2.25 (br s, 2 H); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 169.0, 162.7, 146.3, 142.5, 142.0, 141.5, 140.1, 135.8, 133.1, 129.7, 128.0, 125.8, 125.1, 118.6, 65.5, 47.8, 47.4, 20.5. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.54; H, 4.40.

Reaction between 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-5,8-dione (11) and Tropone. The mixture of dihydroquinone **11** (570 mg, 3.3 mmol) and tropone (420 mg, 4.0 mmol) in 15 mL of xylene was heated at 140 °C for 26 h under nitrogen atmosphere. The solvent was distilled off under reduced pressure, and the residue was chromatographed on a silica gel (20 g) column. After a forerun of the unreacted quinone **11** (300 mg), elution of the column with a 15% ethyl acetate–hexane mixture gave **12** (40 mg, 19.3%), **14** (10 mg, 4.8%), **13a** (115 mg, 55.5%), and quinol **15** (70 mg, mp 190 °C). Compound **12** was recrystallized from a dichloromethane–hexane mixture to furnish yellow crystals: mp 195 °C; IR (KBr) 1640, 1580, 1320, 860 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.20–7.00 (m, 1 H), 6.82 (t, 1 H), 6.52 (t, 1 H), 5.24 (br d, $J = 12$ Hz, 1 H), 5.08–4.88 (m, 1 H), 4.76–4.44 (m, 1 H), 3.48 (br s, 2 H), 2.08–1.08 (m, 6 H); mass spectrum, m/z 278.0 (M^+). Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.69; H, 4.98. Compound **14** was recrystallized from a dichloromethane–hexane mixture to furnish red crystals: mp 210 °C; IR (KBr) 3250, 2650, 2580, 830 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 8.18 (t, $J = 6$ Hz, 1 H), 7.40–7.16 (m, 2 H), 7.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 6.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 5.42 (br s, 1 H), 3.90 (br s, 1 H), 3.60 (br s, 1 H), 2.10–1.24 (m, 6 H); mass spectrum, m/z 278.0 (M^+). Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.83; H, 5.00. Compound **13a** was recrystallized from ethyl acetate: mp 264 °C; IR (KBr) 3250, 1640, 1620, 1300, 840 cm^{-1}. This compound was best characterized as its diacetate **13b** (vide infra).

Acetylation of 13a. The compound **13a** (100 mg, 0.36 mmol) was treated with a mixture of dry pyridine (0.5 mL) and acetic anhydride (2 mL). The reaction mixture was stirred at ambient temperature for 12 h and then poured into cold water (10 mL). The aqueous layer was extracted with ether (3 × 20 mL). The combined ethereal layer was washed with 10% HCl (10 mL), water (10 mL), and finally with brine (15 mL). Drying over anhydrous Na_2SO_4, removal of solvent, and recrystallization of the crude product from a dichloromethane–hexane mixture furnished the pure diacetate **13b** (127 mg, 98.5%): mp 220 °C; IR (KBr) 1760, 1670, 1180, 890 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.22–7.0 (m, 1 H), 6.88 (br t, 1 H), 6.76 (br t, 1 H), 5.24 (br d, $J = 12$ Hz, 1 H), 4.68 (br d, $J = 8$ Hz, 1 H), 4.30 (br t, 1 H), 3.28 (br s, 2 H), 2.40 (s, 6 H), 2.0–1.10 (m, 6 H). Anal. Calcd for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53. Found: C, 72.26; H, 5.41.

Hydrogenation of the Diacetate 13b. The diacetate **13b** (16 mg, 0.044 mmol) was dissolved in ethyl acetate (2 mL) and hydrogenated over 10% palladium–carbon catalyst for 1 h. The catalyst was filtered, and the solvent was removed under reduced pressure to yield the crude product. This was recrystallized from a dichloromethane–hexane mixture to furnish **16** (15 mg, 94%), identical with the sample prepared above through hydrogenatiion of the diacetate **3b**.

Acknowledgment. We thank UGC for support through SAP and COSIST programmes in organic chemistry. S.R.K. thanks CSIR for a research fellowship.

Registry No. 1, 6829-72-7; 2, 119973-17-0; **3a**, 119973-18-1; **3b**, 119973-20-5; **4a**, 119973-19-2; **4b**, 119973-21-6; 5, 3090-47-9; 11, 61632-88-0; 12, 119973-22-7; **13a**, 119973-23-8; **13b**, 119973-26-1; 14, 119973-24-9; 15, 16144-91-5; 16, 119973-25-0; tropone, 539-80-0.

Formation of Thiocarbamates in the Oxidative Condensation of Amines and Organic *N*-Chloroamines with Potassium Ethyl Xanthate

Frank E. Scully, Jr.,* and Teresita Ortega

Department of Chemical Sciences, Old Dominion University, Norfolk, Virginia 23529-0126

Received December 8, 1988

Introduction

We have been investigating new reactions of organic *N*-chloroamines in an effort to develop methods of derivatizing them for analysis in dilute aqueous solution. In a series of papers Smith et al.[1-4] reported that the sulfur moiety of certain thiols, dithiocarbamates, and carbodithioates reacted with organic *N*-chloroamines or with amines in the presence of iodine to form sulfenamide products. Although he examined the reaction of xanthate salts with chloroamines, he failed to characterize the products beyond their inability to accelerate rubber vulcanization. When we reacted *N*-chloropiperidine with the sodium salt of xanthic acid, we expected a sulfenamide product to form. Instead we isolated a thiocarbamate. Subsequently we noted that in a recent patent Giancarlo[5]

(1) Carr, E. L.; Smith, G. E. P.; Alliger, G. *J. Org. Chem.* **1949**, *14*, 921–934.
(2) Smith, G. E. P.; Alliger, G.; Carr, E. L.; Young, K. C. *J. Org. Chem.* **1949**, *14*, 935–945.
(3) Alliger, G.; Smith, G. E. P., Jr.; Carr, E. L.; Stevens, H. P. *J. Org. Chem.* **1949**, *14*, 962–966.
(4) Donia, R. A.; Shotten, J. A.; Bentz, L. O.; Smith, G. E. P., Jr. *J. Org. Chem.* **1949**, *14*, 946–951.

0022-3263/89/1954-2978$01.50/0