creases $\Delta G^{\ddagger}$ and also *decreases* $z_{\ddagger}$; this is Hammond behavior. In contrast, Figure 3a shows how the same value of $\Delta G^{\ddagger}$ (16) can be obtained from the same values of $\Delta G_{NN}^{\ddagger}$ and $\Delta G_{XX}^{\ddagger}$ without averaging them to obtain $\Delta G_{int}^{\ddagger}$; comparison of Figures 1a and 3a demonstrates how replacing the NN reactant parabola with the more gently curved XX parabola while retaining the NN product parabola decreases $\Delta G^{\ddagger}$ and also *increases* $z_{\ddagger}$; this is anti-Hammond behavior.

In addition to this direct anti-Hammond effect, if the change in the reactant parabola is accompanied by a change in $\Delta G°$, then that variation in $\Delta G°$ can result in an opposing Hammond effect. Figure 3b illustrates how large a decrease in $\Delta G°$ would have to be in order for its tendency to decrease $z_{\ddagger}$ to be dominant.

Conclusions

Marcus' rate theory in its conventional form is unable to accommodate anti-Hammond transition-state structural variation in reactions for which $\Delta G° < 0$. One way to extend Marcus' theory to allow it to be consistent with such behavior is to modify the usual assumption that $\Delta G_{int}^{\ddagger}$ is the mean of the two $\Delta G^{\ddagger}$ values for the corresponding symmetric reactions. That assumption is expected to be valid for reactions in which bond breaking and bond making occur synchronously and to equal extents; it should not be valid if those two processes are not in step with one another, and in the limit of complete asynchrony the barrier would be correctly modeled by two intersecting parabolae: one with it force constant equal to that of the bond being broken and the other with its force constant equal to that of the bond being formed. This mode of barrier construction allows anti-Hammond behavior.

Thus, conversely, observations that imply anti-Hammond behavior may be diagnostic of the presence of such an asynchrony. Similar conclusions recently have been reached by other investigators[20-22] via arguments that do not directly involve Marcus' theory. It will be interesting to see whether the surprising implication of such conclusions that even *methyl* transfers can have significant asychrony turns out to be correct.

Acknowledgment. This work was supported in part by Grant CHE83-04874 from the National Science Foundation.

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(20) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1129–1130.

(21) Buncel, E.; Wilson, H.; Chuaqui, C. *J. Am. Chem. Soc.* **1982**, *104*, 4896–4900.

(22) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125–136.

Synthesis and Chemistry of an Unusual Bridgehead Alkene

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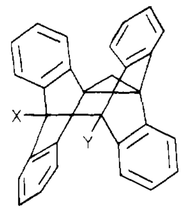
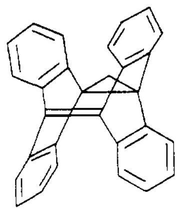
We previously described the preparation of bromide **1a** from photocyclization of (9-bromoanthryl)anthrylmethane,[1] and we also gave a preliminary indication of the dehydrobromination of **1a** to form the bridgehead alkene **2** using the Greene procedure[2] of capture of **2** with azide ion and subsequent amination and oxidation of the resulting triazoline. The preliminary result has now been confirmed and the identity of **2** established by its chemistry and single-crystal X-ray diffraction. The X-ray study gave limited information because the crystals were disordered, with the alkene and cyclopropane units randomly interchanged so that only a mean bridgehead–bridgehead bond distance (1.595 Å) could be determined.

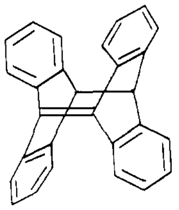


1a, X = Br; Y = H
b, X = I; Y = I
c, X = CH_3; Y = H



2

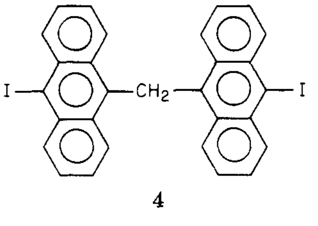
Compound **2** is interesting particularly because of the possibility that the uniquely positioned alkene and cyclopropane rings might interact to affect the rates or products of chemical reactions. The X-ray study showed the double bond carbons and the opposite cyclopropane carbons to be separated by 2.661 Å. Of special value as a model is the simple dehydrodianthracene **3**, prepared earlier by Greene and co-workers.[2,3] The preparation of **3** has been repeated in order to make comparisons.



3

Compound **2** has been found to be qualitatively and quantitatively more reactive than **3**. The reactions discovered for **2** have been reactions of the alkene function only, however, with no transannular participation by the cyclopropane ring in product formation. Iodine, oxygen, and HBr all add to **2** but not to **3**.

The reaction of **2** with I_2 in carbon tetrachloride yields bis(10-iodoanthryl)methane (**4**), in a process markedly accelerated by light and inhibited by isoamyl nitrite. A free-radical chain mechanism is inferred, and a probable intermediate is the bridgehead diiodo compound **1b**. Chlorine and bromine add to **2** to give analogous products.



4

The reaction of **2** with oxygen can be carried out by bubbling oxygen through a carbon tetrachloride solution of **2** at room temperature. The first product is a colorless 1:1 adduct with a mass spectral parent mass at 398 and shows no carbonyl stretching bands in the infrared. The

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(1) Applequist, D. E.; Swart, D. J. *J. Org. Chem.* **1975**, *40*, 1800.

(2) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342.

(3) Weinshenker, N. M.; and Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 506.

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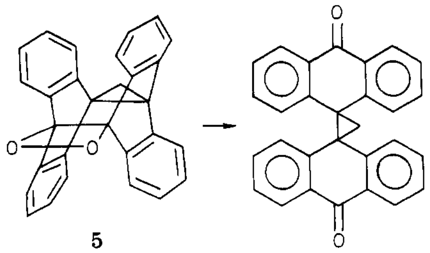
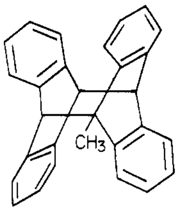
structure **5** is tentatively assigned. The compound isomerizes thermally to a yellow substance, assigned structure **6** from the spectroscopic characteristics, including a carbonyl stretching band at 1685 cm^{-1} and single aliphatic hydrogen peak in the NMR at 3.42 ppm. Reaction of an alkene at room temperature with ground-state oxygen to form an isolable dioxetane does not appear to be a known reaction, although another spontaneous reaction of a bridgehead alkene with oxygen has been reported.[4]



5 **6**

Compound **2** reacted with HBr in dry THF in the dark to give **1a** in 95 percent yield. Under the same conditions **3** gave no reaction. A complex mixture was obtained from **2** and HBr under radical conditions [light and azobis(isobutyronitrile) (AIBN)], leading to the tentative conclusion that the dark reaction is an electrophilic addition process.

In contrast to the greater reactivity shown by **2** as compared with **3** in the free-radical, cycloaddition, and electrophilic reactions cited above, the two show comparable reactivities in the addition of a strongly basic reagent, methylithium. A 1:1:1 mixture of **2**, **3**, and methyllithium in THF at room temperature for 5 min gave a product mixture (after aqueous workup) consisting of unreacted **2**, unreacted **3**, the adduct **1c** from **2**, and the adduct **7** from **3** to the extent of 15%, 35%, 35%, and 15%, respectively.



7

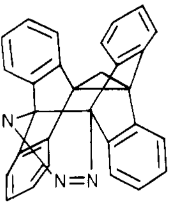
Several additional reactions of **2** have been examined in a preliminary way.[5]

Experimental Section

Melting points were determined by using a Büchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian EM-390 (90 MHz) instrument unless otherwise noted. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on JEOL FX-60 (15 MHz) or Varian XL-100 (25.2 or 250 MHz) instruments and were wide-band decoupled. All chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane used as an internal standard (δ 0). Infrared (IR) spectra were recorded on Beckman IR-12 or Nicolet FT-IR spectrophotometers. All IR absorptions are reported in reciprocal centimeters. Ultraviolet-visible (UV-vis) spectra were recorded on a Cary 14 UV-visible spectrophotometer (the peak values are in nanometers with ϵ values in parentheses). Mass spectra were run on a Varian MAT CH-5 mass spectrometer by J. C. Cook and his associates. Elemental analyses were performed by J. Nemeth and his associates.

All chemicals and solvents were reagent grade and used without further purification unless otherwise noted.

2,3,4-Triaza-6,7:11,12:13,14:15,16-tetrabenzopentacyclo-$[8.2.2.2^{5,8}.0^{1,5}.0^{8,10}]$hexadeca-3,6,11,13,15-pentaene (8). Under argon, a mixture of 3.00 g (0.0270 mol) of potassium *tert*-butoxide and 20.00 g (0.314 mol) of sodium azide in 500 mL of dry (distilled from 4-Å sieves) dimethyl sulfoxide was stirred for 20 min to give a pale yellow solution, to which was added 1.50 g (3.6 mmol) of **1a**.[1] The resulting mixture was stirred for 2 days. The solution was cooled, and to it added 800 mL of water. The resulting mixture was extracted with 300 mL benzene. Water (200 mL) was added to the aqueous phase and the mixture extracted with 250 mL of benzene. This procedure was repeated two more times, the combined benzene extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to leave a yellow solid. Recrystallization from benzene–hexane afforded beige crystals: 1.12 g (88%); mp 152–154 °C dec; ^{1}H NMR (Me$_2$SO-d_6) 2.95 (s, 2 H), 6.75–6.90 (m, 16 H); ^{13}C NMR (Me$_2$SO-d_6) 12.7187, 122.847, 123.875, 125.073, 126.264, 140.357, 144.209, 145.201; IR (KBr) 3430 (m), 3070 (m), 3020 (w), 3000 (w), 1615 (w), 1475 (s), 1450 (s), 1370 (m), 1300 (w), 1150 (w), 1050 (m), 800 (m), 780 (s), 750 (m), 715 (m), 650 (m); UV-vis (CCl_4) 285 sh (555), 262 (3111), 255 (3668). Anal. Calcd for $C_{29}H_{19}N_3$: C, 85.05; H, 4.67; N, 10.26. Found: C, 85.00; H, 4.59; N, 10.11.



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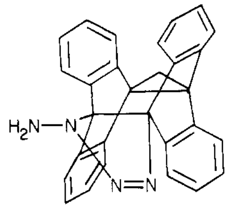

9

***O*-(Mesitylsulfonyl)hydroxylamine.**[6] *tert*-Butyl *N*-(mesitylsulfonoxy)carbamate (4.00 g, 0.0127 mol) was placed in a 125-mL Erlenmeyer flask and cooled to 0 °C. Trifluoroacetic acid (15 mL) was added and the mixture stirred for 5 min. Water (100 mL) was added, and the resulting precipitate was filtered off and dissolved in 10 mL of diethyl ether. Addition of 40 mL of low boiling point petroluem ether caused precipitation of white needles: 2.61 g (95.5%); mp 80 °C dec (lit.[7] mp 80 °C dec); ^{1}H NMR ($CDCl_3$) 2.30 (s, 3 H), 2.61 (s, 6 H), 5.25 (s, 1 H), 6.90 (s, 2 H). Anal. Calcd for $C_9H_{13}NO_3S$: C, 50.22; H, 6.09; N, 6.15. Found: C, 50.20; H, 6.11; N, 6.51.

2-Amino-2,3,4-triaza-6,7:11,12:13,14:15,16-tetrabenzopentacyclo$[8.2.2.2^{5,8}.0^{1,5}.0^{8,10}]$hexadeca-3,6,11,13,15-pentaene (9). To a solution of 1.38 g (0.014 38 mol) of potassium *tert*-butoxide in 60 mL of dry (distilled from Na) dimethoxyethane under argon was added a mixture of 0.60 g (0.00146 mol) **8** in 60 mL of dry DME. The resulting solution was stirred for 1 h, and then to it was added a solution of 1.88 g (0.0087 mol) *O*-(mesitylsulfonyl)hydroxylamine in 15 mL of DME dropwise over 20 min. The resulting mixture was stirred for 24 h and then poured into 200 mL of water. Most of the solvent was removed in vacuo, and the mixture was extracted with four 200-mL portions of benzene. The combined benzene extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a creamy solid. Recrystallization from benzene gave a white powder: 0.50 g (81%); mp 188 °C dec; ^{1}H NMR ($CDCl_3$) 2.80 (s, 2 H), 5.30 (s, 2 H), 6.80–7.12 (m, 16 H); ^{13}C NMR ($CDCl_3$) 13.2085, 42.8706, 53.5080, 71.3328, 85.3644, 124.092, 125.610, 126.515, 126.896, 127.944, 128.472, 131.514, 133.295, 139.933, 142.908, 144.021, 144.671; IR (KBr) 3365 (m), 3245 (s), 3080 (m), 3040 (m), 3015 (w), 1635 (m), 1480 (m), 1455 (s), 1140 (m), 1030 (w), 805 (w); UV-vis (CCl_4) 263 (5700), 257 (6200). Anal. Calcd for $C_{29}H_{20}N_4$: C, 82.05; H, 4.75; N, 13.20. Found: C, 81.98; H, 4.75; N, 13.03.

3,4:8,9:10,11:12,13-Tetrabenzotetracyclo$[5.2.2.2^{2,5}.0^{5,7}]$-trideca[1,3,8,10,12]pentaene (2). Under argon was stirred a suspension of 0.36 g (0.81 mmol) of lead tetraacetate (recrystallized from acetic acid) in 30 mL of dry (distilled from CaH_2) benzene.

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[4] Mattura, M. G.; Adams, R. D.; Wiberg, K. B. *J. Chem. Soc., Chem. Commun.* **1981**, 878.

[5] Suits, J. Z. Ph.D. Thesis, University of Illinois, Urbana, IL, 1982.

[6] Krause, J. G. *Synthesis* **1972**, *3*, 140.

[7] Carpino, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 3133.

To the suspension was added a solution of 0.300 g (0.708 mmol) **9** in 40 mL of dry benzene dropwise over 10 min. The resulting mixture was stirred for 45 min and then filtered. The solvent was removed from the filtrate in vacuo, and the remaining solid was dissolved in a minimum of benzene and placed on a column of 80 g of silica gel [dried at 80 °C (0.05 mmHg) for 4 h] in benzene. Elution with benzene gave a white solid which was washed with hexane and ethyl acetate and then recrystallized from toluene–hexane to give white crystals: 0.1116 g (43.4%); mp 305 °C dec; ^{1}H NMR ($CDCl_3$) 2.72 (s, 2 H), 6.85–7.00 (m, 16 H); ^{13}C NMR ($CDCl_3$) 13.1117, 53.4790, 96.1101, 123.689, 125.305, 125.510, 127.218, 142.329, 146.388; IR (KBr) 3080 (m), 3050 (m), 3015 (w), 1620 (w), 1455 (s), 1140 (m), 940 (w), 765 (s), 650 (m), 609 (m), 510 (m); mass spectrum (10 eV), *m/e* (relative intensity) 368 (4.26), 367 (25.96), 366 (100), 365 (2.75), 364 (1.00), 352 (1.72); UV–vis(CCl_4) 255 (3910), 275 (3257), 285 (2273). Anal. Calcd for $C_{29}H_{18}$: C, 95.05; H, 4.95. Found: C, 95.18; H, 4.97.

An X-ray diffraction study by Scott Wilson gave the structural parameters cited in the discussion. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/C$. Details are reported elsewhere.[5]

9,9′-Dehydrodianthracene (3) was prepared by the method of Weinshenker and Greene[3] in 44% overall yield from di-9-anthrylcarbinol. The properties of **3** were the same as those reported: mp 309 °C (lit.[3] mp 309 °C); NMR ($CDCl_3$) 4.55 (s, 2 H), 6.65–6.85 (m, 16 H).

Reaction of 2 with Iodine. To a solution of 0.0489 g (0.133 mmol) of **2** in 50 mL of CCl_4 was added 0.2152 g (0.923 mmol) of iodine. The resulting solution was stirred for 4 days and then washed with 30 mL of a saturated solution of sodium bisulfite. The aqueous phase was extracted with three 100-mL portions of CCl_4. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a yellow solid, mp 300–301 °C dec. The solid was recrystallized from benzene–hexane to give yellow **4**: 0.0558 g (68%); mp 320–322 °C; ^{1}H NMR ($CDCl_3$) 5.94 (s, 2 H), 7.25–7.60 (m), 7.89–8.05 (m), 8.33–8.42 (m, total area under aromatic region 16 H); IR (KBr) 3070 (w), 3030 (w), 1620 (w), 1530 (m), 1440 (w), 1340 (m), 1300 (w), 1050 (w), 915 (s), 750 (s), 705 (m); UV–vis (CCl_4) 410 (8000), 385 (7500), 365 (6000), 255 (63 000). Anal. Calcd for $C_{29}H_{18}I_2$: C, 56.18; H, 2.93; I, 40.89. Found: C, 56.30; H, 2.93; I, 41.02.

The same product was obtained when the reaction mixture was irradiated with a sunlamp, but reaction times were shortened greatly. Reactions were monitored by NMR analysis. In one series with excess I_2, the half-life for disappearance of **2** was about 270 min in the dark, about 130 min with a sunlamp at 8 ft, and 60 min with the lamp at 1 ft. When 2 equiv of isoamyl nitrite was included in the dark control, the half-life was extended to about 750 min (by extrapolation of data through 570 min).

Reaction of 3 with Iodine. A solution of 0.10 g (0.28 mmol) of **3** in 30 mL of CCl_4 was wrapped in foil, and to it was added 0.20 g (0.85 mmol) of iodine. The resulting solution was stirred for 3 days and then treated with 20 mL of a saturated solution of sodium bisulfite. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give 0.0819 g (82% recovery) of a white solid, the NMR of which was identical with that obtained for **3**.

A solution of 0.10 g (0.28 mmol) **3**, 0.20 g (0.85 mmol) iodine, and 50 mL of CCl_4 was illuminated with a 275-W General Electric sunlamp for 3 days. The solution was worked up as described in the preceding paragraph. A white solid was obtained, the NMR of which showed it to be mostly unreacted **3** with some bianthryl.[3]

Reaction of 2 with Oxygen. A solution of 0.0532 g (0.145 mmol) of **2** in 20 mL of CCl_4 was equipped with an oxygen bubbler, and oxygen gas was bubbled through the solution for 4 days. The solvent was removed from the solution in vacuo to give a yellow solid, which was triturated with ethyl acetate to give a white precipitate and a yellow solution. The solid was dried under high vacuum for several hours to give a white solid: 0.0265 g (46%); mp 180 °C yellow, 240 °C dec; ^{1}H NMR ($CDCl_3$) 2.75 (s, 2 H), 6.75–6.95 (m, 16 H); UV (CCl_4) 285 (1500), 275 (2500), 255 (4500); IR (KBr) 3060 (w), 3040 (w), 1630 (m), 1455 (m), 1280 (w), 935 (w), 865 (m), 670 (s); mass spectrum (10 eV) *m/e* (relative intensity) 398 (0.77), 383 (4.26), 382 (11.30), 381 (2.22), 367 (36.56), 366 (100), 365 (16.26), 364 (6.81), 353 (3.12), 352 (3.18), 351 (6.16), 350 (7.05); mass spectrum (70 eV), *m/e* (relative intensity) 383 (1.27), 382 (3.19), 381 (0.68), 368 (3.93), 367 (11.81), 366 (31.37), 365 (8.09), 353 (1.59), 352 (1.90), 350 (4.64), 45 (2.72), 44 (100), 43 (24.34). Anal. Calcd for $C_{29}H_{18}O_2$: C, 87.42; H, 4.55. Found: C, 89.44; H, 4.78. Recrystallization from ether or sublimation at 100 °C (0.05 mmHg) gave a yellow material the NMR of which was the same as that obtained for **6** (see below).

The structure of the white solid is assigned as **5**.

The solvent was removed from the filtrate to give a yellow solid, which was placed on a column of silica gel in benzene and eluted with benzene to give 0.0030 g of a yellow solid, mp 283–284 °C (anthraquinone, mp 283.5–285 °C). Anal. Calcd for $C_{14}H_8O_2$: C, 80.76; H, 3.87. Found: C, 80.97; H, 3.81.

The eluent was changed to ether and a yellow solid was obtained which was dried under high vacuum for several hours to give a yellow solid: 0.0241 g (45%); mp 240 °C dec; ^{1}H NMR ($CDCl_3$) 3.42 (s, 2 H), 7.45–8.30 (m, total area 16 H); IR ($CHCl_3$) 3010 (m), 1685 (s), 1600 (m), 1450 (w), 1315 (m), 1285 (m), 1215 (s), 1210 (s), 935 (w); UV ($CHCl_3$) 280 (16 700), 255 (16 100); mass spectrum (70 eV), *m/e* (relative intensity) 399 (0.23), 398 (0.85), 397 (1.05), 396 (1.47), 382 (1.22), 381 (0.66), 339 (1.11), 279 (1.08), 225 (1.22), 224 (4.88), 223 (5.98), 222 (26.62), 221 (16.92), 211 (1.12), 210 (7.88), 209 (20.97), 208 (100), 207 (16.59), 206 (15.88), 205 (1.28), 195 (6.97), 194 (41.27), 193 (25.60), 192 (1.95), 191 (1.34), 182 (1.64), 181 (18.03), 180 (94.34), 179 (17.38), 178 (19.16), 167 (2.01), 166 (11.37), 165 (59.48), 164 (13.62), 163 (15.77). Sublimation at 100 °C (0.05 mmHg) gave an analytical sample. Anal. Calcd for $C_{29}H_{18}O_2$: C, 87.42; H, 4.55. Found: C, 87.37; H, 4.80.

The structure of the material is tentatively assigned as **6**.

Isomerization of 5. A small amount of **5** was placed in a beaker and heated at 160 °C for several hours. A yellow material was obtained; mp 240 °C dec. The NMR and IR spectra of the material matched those obtained for **6**.

Effect of Added Inhibitor or Initiator in the Reaction of 2 with Oxygen. A solution of approximately 100 mg of **2** in 50 mL of CCl_4 was prepared and BHT or AIBN added as indicated. The solution was placed in a round-bottomed flask equipped with a condenser, oxygen bubbler tube, and rubber septum. Oxygen was bubbled through the solution over several days. Analyses were made by withdrawing 4-mL aliquots periodically, removing the solvent in vacuo, and obtaining an NMR spectrum of the material in $CDCl_3$. The amount of **6** was determined by measuring the relative peak intensities at 3.45 (**6**) and 7.15 ppm ($CHCl_3$). Where the amount of anthraquinone was determined, the solvent was removed from the NMR sample, and the solid was dissolved in 50 mL of CCl_4 and placed in a UV spectrophotometer. The anthraquinone content was determined by measuring the absorbance at 330 nm (ϵ 4500).

Neither BHT nor AIBN had any significant effect on the rate of formation of **6**, but the BHT did completely suppress the formation of anthraquinone.

Reaction of 2 with Anhydrous Hydrogen Bromide in the Dark. A flask containing a solution of 0.0438 g (0.120 mmol) of **2** in 50 mL of dry (distilled from sodium–benzophenone) THF was wrapped in foil and saturated with hydrogen bromide gas. The mixture was stirred for 3 days, after which time 10 mL of 20% sodium bicarbonate solution was added to the mixture. THF was removed in vacuo and the aqueous residue extracted with four 50-mL portions of benzene. The combined benzene extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a creamy solid, which was washed with ether and dried under high vacuum for several hours to give 0.0518 g (95%) of white solid **1a**, mp 270–272 °C dec. The IR and NMR spectra were identical with those of **1a**.

When a similar reaction was run with added AIBN and under illumination for 3 days, a complex product mixture containing comparable amounts of **1a**, the dihydro derivative of **2** (**1**, X = Y = H), and bis(10-bromo-9-anthryl)methane, identical with the bromine addition product of **2**,[5] was obtained.

Compound **3** did not react with HBr, even under illumination with AIBN, (88 percent recovery of **3** after three days of irradiation).

A control showed that **1a** was not affected by irradiation with AIBN and HBr in THF.

9-Methyldianthracene (7). A solution of 1.00 g (5.6 mmol) of anthracene, 1.10 g (5.73 mmol) of 9-methylanthracene, and 50 mL of benzene was deoxygenated by purging with nitrogen for several minutes and then irradiated under nitrogen by using a General Electric 275-W sunlamp. After 3 days, a precipitate was filtered off and the solvent removed from the filtrate in vacuo, leaving a white solid which was recrystallized twice from benzene to give a white solid: 0.46 g (22%); mp 220 °C dec; 150–160 °C remelt (lit.[8] mp 220 °C dec, 155–180 °C remelt). Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 93.98; H, 5.99.

Reaction of 2 with Methyllithium. To a solution of 0.10 g (0.27 mmol) of **2** in 50 mL of dry (distilled from Na) THF was added 0.20 mL (0.30 mmol) of a 1.5 M solution of methyllithium in ether. The resulting mixture was stirred for 2 h and then treated with 10 mL of water. The solvent was removed in vacuo and the residue partitioned between 50 mL of water and 50 mL of benzene. The layers were separated, and the aqueous phase was extracted with four 150-mL portions of benzene. The combined organic extracts were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a creamy solid (**1c**): 0.0956 g (92%); mp 255–257 °C; ^1H NMR ($CDCl_3$) 2.15 (s, 3 H), 2.72 (s, 2 H), 4.00 (s, 1 H), 6.65–6.95 (m, 16 H); IR (KBr) 3080 (w), 3040 (w), 3020 (w), 2990 (w), 2910 (w), 1630 (m), 1450 (m), 1375 (m), 1310 (w), 1130 (w), 1005 (w), 935 (w), 810 (m), 750 (m), 685 (m), 660 (m); UV (CCl_4) 285 (2500), 275 (3500), 266 (4400), 255 (7000); mass spectrum (10 eV), m/e (relative intensity) 384 (4.74), 383 (34.35), 382 (100), 381 (4.60), 380 (1.23), 369 (5.65), 368 (26.51), 367 (32.09), 366 (11.09), 365 (5.22), 364 (1.66), 353 (5.76), 352 (5.48), 205 (37.00), 192 (6.05), 191 (19.30), 92 (11.87), 91 (21.95). Recrystallization from benzene–hexane gave an analytical sample. Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.89; H, 5.76.

Reaction of 3 with Methyllithium. To a solution of 0.15 g (0.42 mmol) of **3** in 50 mL of dry THF was added 1.0 mL (0.67 mmol) of a 1.5 M solution of methyllithium in ether. The resulting solution was stirred for 1 h and then treated with 30 mL water. A workup as described for the preceding reaction gave a white solid: 0.0763 g (49%); mp 220 °C dec (9-methyldianthracene, lit.[8] mp 220 °C dec, 155–180 °C remelt); ^1H NMR ($CDCl_3$) 2.08 (s, 3 H), 3.86 (s, 1 H), 4.45 (s, 2 H), 6.70–6.85 (m, 16 H), identical with that of the authentic sample. Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 94.22; H, 5.97.

Competitive Reaction of 2 and 3 with Methyllithium. To a solution of 0.0112 g (0.0305 mmol) of **2**, 0.0114 g (0.0321 mmol) of **3** and 10 mL of dry (distilled from sodium–benzophenone) THF under nitrogen was added by syringe 0.017 mL (0.03 mmol) of a 1.8 M solution of methyllithium in ether. The resulting solution was stirred for 5 min and then treated with 10 mL of water. The THF was removed in vacuo and the residue partitioned between 30 mL of benzene and an additional 10 mL of water. The layers were separated, and the aqueous layer was extracted with 50 mL of benzene. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a white solid which was dried under high vacuum for several hours: ^1H NMR ($CDCl_3$, relative intensities) 2.08 (s, 9), 2.15 (s, 21), 2.72 (s, 20), 3.86 (s, 3), 4.00 (s, 7), 4.45 (s, 6), 4.55 (s, 14), 6.6–7.1 (m, 320).

The aromatic absorptions for **1c**, **2**, **3**, and **7** all occurred in the same region (6.6–7.1 ppm). Peak assignments for the remainder of the spectrum are as follows: 2.08 (CH_3, **7**), 3.86 (bridgehead proton at C-10′, **7**), 4.45 (bridgehead protons at C-9′ and C-10, **7**), 2.15 (CH_3, **1c**), 2.72 (cyclopropyl protons, **1c**), 4.00 (bridgehead proton, **1c**), 2.72 [cyclopropyl protons, **2** (could not be separated from cyclopropyl protons of **1c**)], 4.55 (bridgehead protons, **3**).

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Registry No. **1a**, 55043-43-1; **1c**, 87568-72-7; **2**, 19770-71-9; **3**, 17938-63-5; **4**, 87568-73-8; **5**, 87568-74-9; **6**, 72423-84-8; **7**, 87568-75-0; **8**, 87568-76-1; **9**, 87568-77-2; *O*-(mesitylsulfonyl)hydroxylamine, 36016-40-7.

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[8] Applequist, D. E.; Litle, R. L.; Friedrich, E. C.; Wall, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 452.

Structure of Teucroxide. Application of Natural-Abundance ^{13}C–^{13}C Coupling Constants Observed via Double-Quantum Coherence

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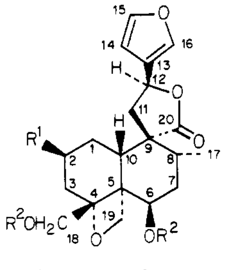
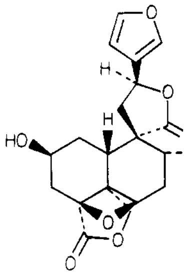
The neoclerodane diterpenoids of *Teucrium chamaedrys L.* (Labiatae) have been the subject of a number of investigations.[2] Now we have isolated from this plant a new neoclerodane diterpenoid, teucroxide, the structure of which (**1**) was established mainly by ^1H and ^{13}C NMR spectroscopic studies.

Combustion analysis and mass spectrometry indicated the molecular formula $C_{20}H_{26}O_7$ for teucroxide (**1**). Its IR spectrum was consistent with the presence of a furan ring (3150, 3130, 3120, 1600, 1508, 880 cm^{-1}), a γ-lactone group (1760 cm^{-1}), and hydroxyl groups (3460, 3360, 3290 cm^{-1}). The presence of three hydroxyl groups was established by the formation, on treatment with Ac_2O–pyridine, of a triacetate, $C_{26}H_{32}O_{10}$ (**2**), the IR spectrum of which showed no OH absorption.



1, $R^1 = OH$; $R^2 = H$
2, $R^1 = OAc$; $R^2 = Ac$
4, $R^1 = R^2 = H$
5, $R^1 = H$; $R^2 = Ac$



3

The most important information for the structural elucidation of the new clerodane type diterpene **1** was provided by its ^1H NMR spectrum and by that of its triacetyl derivative **2**. Effectively, these spectra (Table I) showed typical signals of a secondary methyl group, a β-substituted furan ring, and a C(20)–C(12*S*) lactone grouping identical with those previously found in several neoclerodane diterpenoids.[2] An AB system at δ 4.57 and 3.76 (J = 12 Hz) in the ^1H NMR spectrum of teucroxide (**1**) (solvent, pyridine-d_5) was attributed to the C(18) hydroxymethylene grouping, which on acetylation appeared at δ 4.14 and 4.07 (solvent, $CDCl_3$) or at δ 4.51 and 4.44 (solvent, C_6D_6) in

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[2] (a) Popa, D. P.; Reinbol'd, A. M. *Khim. Prir. Soedin.* **1972**, *8*, 67. (b) Popa, D. P.; Reinbol'd, A. M. *Ibid.* **1973**, *9*, 31. (c) Popa, D. P.; Reinbol'd, A. M.; Rezvukhin, A. I. *Ibid.* **1973**, *9*, 169. (d) Popa, D. P.; Reinbol'd, A. M. *Ibid.* **1974**, *10*, 321. (e) Reinbol'd, A. M.; Popa, D. P. *Ibid.* **1974**, *10*, 589. (f) Papanov, G. Y.; Malakov, P. Y. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35*, 764. (g) Savona, G.; Garcia-Alvarez, M. C.; Rodriguez, B. *Phytochemistry* **1982**, *21*, 721. (h) Eguren, L.; Perales, A.; Fayos, J.; Rodriguez, B.; Savona, G.; Piozzi, F. *J. Org. Chem.* **1982**, *47*, 4157. (i) Fernandez-Gadea, F.; Pascual, C.; Rodriguez, B.; Savona, G. *Phytochemistry*, in press.

0022-3263/83/1948-5123$01.50/0