3500–2700, 1660, 1580, 1430, 1310, 1250.

25 was formed in a yield of 7% (40 mg). This compound was identical with that reported in the literature.[3a]

2-Carbomethoxy-3-bromo-1,4-dihydro-1,4-ethenonaphthalene (23). The acid **22** (277 mg, 1 mmol) was esterified with diazomethane and the derived ester was purified by filtration through a short silica gel (5 g) column: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.7–7.3 (m, 4 H), 6.9 (t, 2 H), 5.5 (t, 1 H), 4.95 (t, 1 H), 3.7 (s, 3 H); IR (NaCl, film, cm^{-1}) 3080, 2960, 1720, 1620, 1590, 1440, 1320, 1310, 1250.

Acknowledgment. We are indebted to Atatürk University (Grant 1987/40) and the Department of Chemistry for financial support of this work and express our appreciation to Prof. E. Vogel, Dr. H. Schmickler (University of Cologne), Prof. Dr. A. de Meijere (University of Hamburg), and Prof. Dr. M. Schlosser (University of Lausanne) for ^{13}C NMR and mass spectral measurements and Mr. Sahmettin Yildiz for technical assistance.

Registry No. (±)-**6**, 117269-28-0; (±)-**7**, 117404-71-4; (±)-**8**, 117269-29-1; **9**, 117404-72-5; (±)-**10**, 117405-97-7; (±)-**11**, 117269-30-4; (±)-**12**, 117269-31-5; **13**, 54143-22-5; (±)-**14**, 117404-73-6; (±)-**15**, 117404-74-7; (±)-**16**, 117269-32-6; (±)-**17**, 117269-33-7; **19**, 13351-26-3; **20**, 117269-34-8; (±)-**21**, 117269-35-9; (±)-**22**, 117269-36-0; (±)-**23**, 117269-37-1; (±)-**25**, 117269-38-2.

Lewis Acid Promoted Reactions of Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones with Ethyl Diazoacetate[1]

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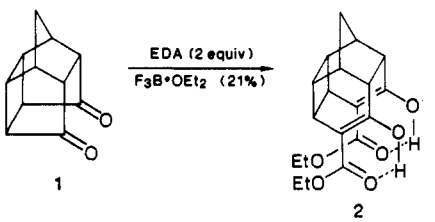
Reaction of 1-X-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones [X = CH_3 (**3**), phenyl (**4**), *p*-cyanophenyl (**9**), and *p*-methoxyphenyl (**13**)] with 1 equiv of EDA in the presence of $F_3B{\cdot}OEt_2$ affords the corresponding monohomologation products [**5** (25%), **6** (25%), **10** (61%), and **14** (37%), respectively]. The structures of **5**, **6**, **10**, and **15** (the product formed via decarboxylation of **14**) were determined by single-crystal X-ray structural analysis. Reaction of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**1**) with 1 equiv of ethyl diazoacetate (EDA) in the presence of boron trifluoride etherate affords ethyl 2,6-dioxopentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane-3-carboxylate (**16a**, 21%) as the major monohomologation product along with ethyl 4,10-dioxotetracyclo[6.4.0.0^{2,6}.0^{5,9}]dodec-11-ene-11-carboxylate (**19**, 17%). Decarboxylation of **16a** with NaCl–DMSO afforded **17** (79%). Subsequent Friedlaender condensation of **17** with *o*-aminobenzaldehyde in the presence of base afforded **18** (73%). The structure of **18** was established by single-crystal X-ray structural analysis.

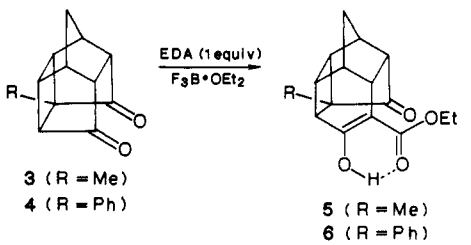
As part of a program designed to explore the synthesis and chemistry of novel functionalized polycyclic cage molecules,[2] we recently reported the results of a study of the Lewis acid promoted reaction of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (PCUD-8,11-dione, **1**) with ethyl diazoacetate (EDA).[3] A single, substituted pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridecane, **2** (Scheme I), was isolated from the reaction of **1** with 2 equiv of EDA in the presence of boron trifluoride etherate. The structure of **2** was established via single-crystal X-ray structural analysis.[3]

In an effort to extend this reaction to synthesize new derivatives of the pentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane ring system, we have undertaken a study of the corresponding boron trifluoride promoted reaction of unsymmetrically substituted PCUD-8,11-diones (i.e., **3** and **4**, Scheme II) with 1 equiv of EDA.[4] In each case, a single monohomologation product was isolated. Not surprisingly, the less hindered of the two carbonyl groups in both **3** and **4** suffered attack by EDA. However, the regiochemistry of the ring-expanded products (**5** and **6**, respectively) thereby obtained in each case is *opposite* of that which we reported earlier[3] for the corresponding bishomologation product, which is formed when **1** is reacted with 2 equiv of EDA in the presence of boron trifluoride etherate. Confirmation of the structures of ring-expanded products **5** and **6** (which served to define the regiochemistry of homologation) was obtained via single-crystal X-ray structural analysis (vide infra).

Scheme I



Scheme II



In the light of our previously published observation[3] regarding the regiochemistry of EDA–$F_3B{\cdot}OEt_2$-promoted

(1) Dedicated to Professor Michael J. S. Dewar on the occasion of his 70th birthday.

(2) Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT, Vol. 1, in press.

(3) Marchand, A. P.; Arney, B. E., Jr.; Gilardi, R.; Flippen-Anderson, J. L. *J. Org. Chem.* **1987**, *52*, 3455.

(4) Marchand, A. P.; Annapurna, G. S. *Abstracts of Papers*; 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 30–Sept 4, 1987; American Chemical Society: Washington, DC, 1987; Abstr ORGN 9.

0022-3263/89/1954-0187$01.50/0

Table I. Crystal Data, Data Collection, and Refinement for 5, 6, 10, 15, and 18

	5	6	10	15	18
formula	$C_{16}H_{18}O_4$	$C_{21}H_{20}O_4$	$C_{22}H_{19}O_4N$	$C_{19}H_{18}O_3$	$C_{19}H_{15}ON$
size, mm	0.20 × 0.60 × 0.80	0.30 × 0.30 × 0.33	0.50 × 0.18 × 0.48	0.20 × 0.20 × 0.40	0.13 × 0.18 × 0.23
M_r	274.32	336.39	361.40	294.35	273.14
	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
	$P2_1/n$	$C2/c$	$Pbcn$	$P2_12_12_1$	$P2_1/n$
a, Å	11.084 (3)	30.855 (4)	24.285 (4)	10.790 (2)	10.525 (3)
b, Å	8.246 (2)	7.246 (1)	10.909 (2)	10.889 (2)	6.556 (2)
c, Å	14.789 (3)	15.180 (2)	13.591 (3)	12.442 (2)	19.447 (4)
β, deg	95.11 (1)	96.00 (2)			103.70 (2)
V, Å^3	1346.3 (5)	3375.6 (7)	3600.4 (10)	1462.2 (4)	1303.7 (5)
a	$35.98 \leq 2\theta \leq 46.97$	$34.18 \leq 2\theta \leq 38.45$	$34.30 \leq 2\theta \leq 39.03$	$3.0 \leq 2\theta \leq 45.0$	$19.16 \leq 2\theta \leq 26.18$
Z	4	8	8	4	4
D_x, g cm^{-3}	1.353	1.324	1.333	1.337	1.393
$F(000)$	584	1424	1520	624	576
μ (cm^{-1})	0.90	0.85	0.86	0.83	0.80
no. I	2372	2973	2351	1125	1697
b	$-13 < h < 13, 0 < k < 9, 0 < l < 17$	$-36 < h < 36, 0 < k < 8, 0 < l < 18$	$0 < h$ 25, $0 < k < 11, 0 < l < 14$	$0 < h < 9, 0 < k < 11, 0 < l < 13$	$-11 < h < 10, 0 < k < 7, 0 < l < 20$
$I > 3\sigma(I)$	1539	1636	1641	848	1182
R, R_w[c]	0.0511, 0.0602	0.0476, 0.0493	0.0495, 0.0470	0.0412, 0.0405	0.0624, 0.0458
g[c]	0.00066	0.00151	0.00057	0.00141	
S	2.162	1.057	1.262	0.891	1.785
$(\Delta/\sigma)_m$	0.009	0.023	0.033	0.012	0.013
d	0.38, −0.31	0.15, −0.19	0.17, −0.20	0.12, −0.14	0.26, −0.25

[a] Twenty-five reflections in the range indicated used for determination of unit cell parameters. [b] Range of hkl values for data collections. [c] $\sum w(|F_o| - |F_c|)^2$ function minimized with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. [d] Maximum and minimum electron densities in the final difference maps (e Å^{-3}).

bishomologation of 1 (Scheme I), the results cited above appear to suggest that a relatively minor structural change at a position removed from the reaction center (i.e., that which is produced via introduction of a substituent at the 1-position in the PCUD-8,11-dione substrate) produces a remarkable switch in the regiochemistry of ketone homologation in this system. If we accept this inference as a working hypothesis, then it is clearly of interest to probe the nature of this substituent effect (i.e., whether it is electronic or steric in origin). In an effort to probe the importance of the electronic effect of the 1-substituent in this regard, 1-(4′-cyanophenyl)- and 1-(4′-methoxyphenyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**9** and **13**, respectively) were synthesized by using the method outlined in Scheme III, and their respective monohomologations with EDA–F_3B·OEt_2 were studied. In the case of **9** as substrate, evidence was sought for the operation of an electron-withdrawing substituent effect by the *p*-cyano group, which might result in some alteration of the regioselectivity of the ketone homologation process. Similarly, it was hoped that the *p*-methoxy group in **13** would exert an electron-donating effect that might affect the regiochemical course of the reaction.

In each case, we isolated a single monohomologation product (i.e., **10** and **14**, respectively) from reaction of **9** and of **13** with 1 equiv of EDA–F_3B·OEt_2. The structure of ring-expanded product **10** was determined via single-crystal X-ray structural analysis. However, in the case of **14**, we were unable to obtain a crystal of sufficient quality to permit its structure to be determined directly via single-crystal X-ray structural analysis. Instead, this material was decarboxylated, thereby affording the corresponding pentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecanedione (**15**; see the Experimental Section). A suitable single crystal of **15** was obtained with which X-ray structural analysis was performed successfully.

The regiochemistry of the product formed via monohomologation of **9** and of **13** is the *same* as that which was obtained for the corresponding monohomologation of **4**. Hence, we conclude that the regiochemistry of monohomologation is not affected by altering the electron-donating or -withdrawing capability of the 1-phenyl substituent in the substituted PCUD-8,11-dione employed as substrate.

X-ray Crystallographic Studies. Information concerning the crystals, methods of data collection, and methods of data refinement for compounds **5**, **6**, **10**, and **15** is given in Table I. The structural parameters among these four compounds display little variation. Compounds **5**, **6**, and **10** exist in the enol form with an intramolecular hydrogen bond between O(2) and the carbonyl oxygen in the ester moiety. The three O···O distances range from 2.561 (2) to 2.612 Å for the three structures. The cyclobutane ring in **5**, **6**, **10**, and **15** is slightly trapezoidal with three sides equivalent and averaging 1.544 (5) Å, while the fourth side [i.e., C(1)–C(7)] is significantly longer with an average value of 1.587 (5) Å.

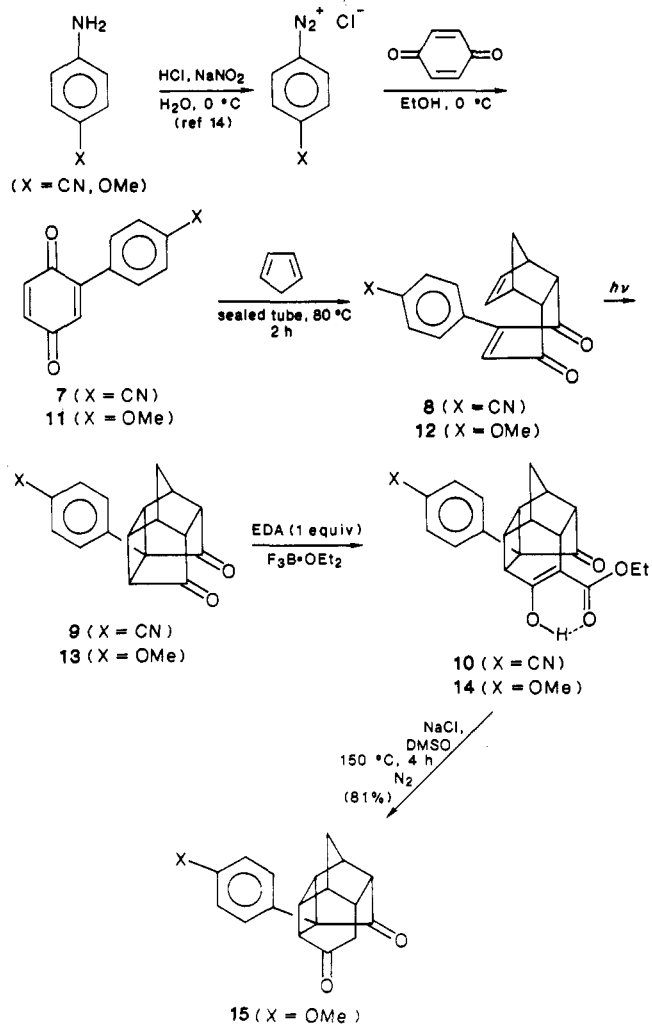
The cyclohexene ring in these compounds exhibits an unusual monoplanar conformation with a torsion angle sequence of --+0+ and is best described as a boat conformation with one side twisted away from being parallel with the other. In each case, this unusual conformation is stabilized by the fact that the cyclohexene ring is fused both to a cyclobutane ring and to a norbornane moiety. The cyclopentane ring, which is opposite to the cyclohexene moiety, exists in an envelope conformation.

The norbornane moiety has a noncrystallographic mirror plane that passes through the C(8)–C(12) and C(4)–C(5) bonds and the methylene bridge. The average bond lengths across this pseudomirror plane are statistically equivalent; however, the C(4)–C(5) bond length [average value 1.580 (1) Å] is significantly longer than the C(8)–C(12) bond length [average value 1.543 (5) Å]. This discrepancy results from the fact that the C(8)–C(12) bond is also contained within a cyclobutane ring.

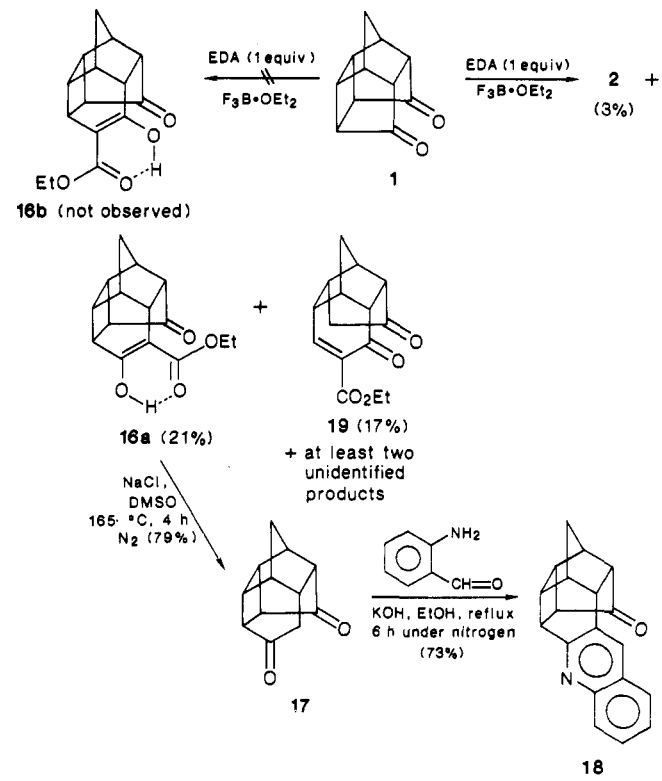
The structures of **5**, **6**, and **10** are reasonably well reproduced by molecular mechanics calculations.[5] The calculated angles differ by an average of 0.8° from the

(5) (a) Allinger, N. L.; Yuh, Y. H. 1980, MM3 and MMPI subroutines for IBM PC. Updated by Rohren, L. C. (1984); adapted by Gajewski, J. J.; Gilbert, K. E. from copy supplied by Nelson, O.; Owen, C. S. Obtained from Serena Software, 489 Serena Lane, Bloomington, IN 47401. (b) Tables of selected bond distances and valence angles for **5**, **6**, and **10** (average values and MM2 calculated values) are given in the supplementary material.

Scheme III



Scheme IV



average of the experimental values. The trends among calculated bond lengths are consistent with those observed. However, several of the calculated bond lengths are significantly shorter than the observed values, a result that indicates the need for parameter adjustment in these strained systems. The heat of formation and strain energy for **5** (with the ester group replaced by a CO_2H group for computational purposes) are −136.2 and 41.6 kcal/mol, respectively. Some mixing of orbitals undoubtedly occurs in these strained systems with concomitant significant shifts in bond lengths. Calculated and averaged torsion angles differ by an average of 2° in **5**, **6**, and **10**.

Discussion

The apparent lack of sensitivity of the monohomologation reactions of **4**, **9**, and **13** to electronic effects of para substituted 1-phenyl groups in these substrates was a cause of some concern. Accordingly, as a precautionary measure, we decided to reinvestigate the reaction of **1** with EDA in the presence of boron trifluoride etherate. Since the structure of the bishomologation product, **2**, is known with certainty, it was tacitly assumed at the outset of this study that the reaction of **1** with 1 equiv of EDA in the presence of boron trifluoride etherate would afford a monohomologation product, **16b**, with the same regiochemistry as that found in both of the expanded rings in **2**. In fact, this is *not* the case. The reaction of **1** with 1 equiv of EDA–$F_3B{\cdot}OEt_2$ afforded **2** (3%), a pentacyclic monohomologation product (21%), and a tetracyclic compound (**19**, 17%),[6] along with at least two other minor products that were not characterized (see Scheme IV). The monohomologation product, mp 95–97 °C, that was isolated from this reaction was found to be **16a** (Scheme IV), which possesses the *same* regiochemistry as do **5**, **6**, **10**, and **14**! The fact that this product is **16a** and not **16b** was demonstrated via the reaction sequence shown in Scheme IV (i.e., decarboxylation[7] of **16a** afforded cage diketone **17**, which was then converted into **18** via base-promoted Friedlaender condensation[8] with *o*-aminobenzaldehyde). The structure of **18** was established unequivocally via single-crystal X-ray structural analysis.

A possible explanation for this apparent anomaly may lie in the relative stabilities of the two possible monohomologation products. Present evidence suggests that both monohomologation products are formed in this reaction. When a second equivalent of EDA is present, **16b** is trapped, thereby affording the corresponding bishomologation product, **2**. If instead we attempt to *isolate* the monohologation products, **16a** is stable to the workup and isolation procedure, whereas apparently **16b** is not. Compound **16b** eventually may suffer retro-Michael reaction with concomitant cleavage of a cyclobutane ring carbon–carbon σ-bond, thereby affording **19** (Scheme IV).

As a first step toward understanding the mechanism of the ring expansions **3** → **5**, **4** → **6**, **9** → **10**, **13** → **14**, and **1** → **16a**, it is instructive to consider possible transition states in these systems. One such approach to this problem, which focuses upon relative conformational energetics in diastereoisomeric EDA adducts,[9,10] is shown in Scheme V. Here, it is assumed that (i) for steric reasons, EDA

(6) The structure of **19** has been established by single-crystal X-ray structural analysis (Watson, W. H.; Nagl, A.; Marchand, A. P.; Vidyasagar, V. Unpublished results).

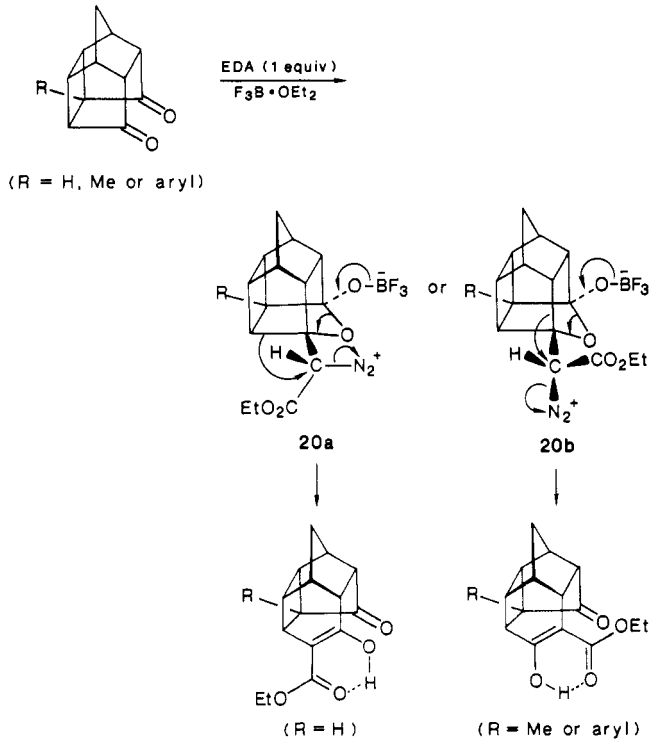
(7) (a) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, 957. (b) Krapcho, A. P.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Short, F. W. *Tetrahedron Lett.* **1974**, 1091.

(8) (a) Caluwe, P. *Tetrahedron* **1980**, *36*, 2359. (b) Thummel, R. P.; Lim, J.-L. *Tetrahedron Lett.* **1987**, *28*, 3319.

(9) Mock, W. L.; Hartman, M. E. *J. Org. Chem.* **1977**, *42*, 466.

(10) Dave, V.; Warnhoff, E. W. *J. Org. Chem.* **1983**, *48*, 2590.

Scheme V



preferentially attacks the exo face of the least hindered [C(8)] carbonyl group in **3**, **4**, **9**, **13**, and **1**, (ii) carbon–carbon bond migration in the resulting EDA adduct occurs exclusively antiperiplanar with respect to the leaving group (i.e., N_2^+),[9] and (iii) the preferred configuration of attack by EDA will result in the formation of that conformer that minimizes nonbonded interactions between the CO_2Et group and the bulk of the cage moiety in the substrate. Given these assumptions, attention can then be focused upon just two diastereoisomeric transition states, i.e., **20a** and **20b** (Scheme V).

Dave and Warnhoff[10] employed similar considerations in an effort to rationalize the observed course of regiospecific homologations of unsymmetrical cyclic and noncyclic ketones with EDA–boron trifluoride etherate. These investigators found that when α-halo ketones were employed as substrates, the presence of the halogen atom effectively suppressed migration of the terminus to which it was attached, thereby resulting in regiospecific monohomologation of the substrate. The authors ascribed their observations to the electron-withdrawing effect of the α-halogen. However, in another study of EDA–F_3B·OEt_2-promoted monohomologation of unsymmetrically substituted cycloalkanones, Liu and Majumdar[11] found that the reaction was controlled by steric factors, i.e., the major product generally resulted via preferential migration of the *less substituted* of the two α-carbon atoms.

Without recourse to detailed quantum mechanical and/or molecular mechanics calculations, we cannot be certain of the mechanism by which the electronic and/or steric nature of the substituent in the 1-position of PCUD-8,11-dione influences the relative accessibilities of transition states **20a** and **20b** in this reaction. Additional experiments that are designed (i) to clarify the regiochemistry of the reaction of **1** with EDA (1 equiv) in the presence of boron trifluoride etherate and (ii) to provide further insight into the nature of the transition state in the EDA–F_3B·OEt_2-promoted monohomologation of substituted PCUD-8,11-diones are in progress.

(11) Liu, H. J.; Majumdar, S. P. *Synth. Commun.* **1975**, *5*, 125.

Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry at the University of Nebraska, Department of Chemistry, Lincoln, NE.

Reaction of 3 with EDA–F_3B·OEt_2. A suspension of diketone **3**[12] (2.0 g, 10.6 mmol) in anhydrous ether (100 mL) was cooled to 0 °C by application of an external ice bath. Boron trifluoride etherate (1.3 mL, 11 mmol) was slowly added with stirring to the cooled reaction mixture. After all of the Lewis acid had been added, EDA (1.21 g, 10.6 mmol) was added slowly with stirring to the cooled reaction mixture. After all of the EDA had been added, the stirred reaction mixture was allowed to warm gradually to room temperature. The reaction mixture was stirred at room temperature for 2 h and then quenched by addition of saturated aqueous sodium bicarbonate solution (100 mL). The ether layer was separated, and the aqueous layer was extracted with methylene chloride (100 mL). The combined organic layers were washed with water (100 mL), dried (anhydrous sodium sulfate), and filtered, and the filtrate was concentrated in vacuo. The crude residue thereby obtained (3.3 g) was purified by column chromatography (silica gel stationary phase, 15% ethyl acetate–hexane mixed solvent as eluent). Pure **5** (0.7 g, 25%) was thereby obtained as a colorless microcrystalline solid: mp 131 °C; IR (KBr) 1715 (s), 1625 (s), 1415 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.21 (t, J = 7.2 Hz, 3 H), 1.50 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.75 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.1 (br s, 2 H), 2.48–2.75 (m, 3 H), 2.85 (s, 1 H), 2.95 (s, 1 H), 3.40–3.50 (m, 3 H), 4.15 (q, J = 7.2 Hz, 2 H), 11.8 (br s, 1 H): ^{13}C NMR ($CDCl_3$) δ 13.98 (q), 17.32 (q), 33.98 (d), 37.28 (t), 40.41 (d), 41.44 (d), 43.16 (d), 43.44 (d), 45.01 (d), 54.08 (s), 54.99 (d), 60.27 (t), 99.24 (s), 170.35 (s), 173.57 (s), 216.78 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 202 (37.7), 132 (53.2), 107 (100). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.07; H, 6.57. Found: C, 70.32; H, 6.73.

Continued elution of the chromatography column afforded a mixture of products (1.2 g), which resisted further attempts at separation and purification. The mixture of products thereby obtained was not characterized.

1-Phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (4). A solution of 6-phenyl-1,4α,4aα,5α,8β,8aα-hexahydro-1,4-methanonaphthalene-5,8-dione (synthesized via Diels–Alder cycloaddition of cyclopentadiene to 2-phenyl-*p*-benzoquinone,[13] 3.5 g, 14 mmol) in acetone (500 mL) was purged with nitrogen and then was irradiated under nitrogen for 7 h with a 450-W Hanovia medium-pressure mercury lamp (Pyrex filter). At the conclusion of the photolysis, the reaction mixture was concentrated, and the residue was recrystallized from acetone. Pure **4** (3.0 g, 86%) was thereby obtained as a colorless microcrystalline solid: mp 134–135 °C; IR (KBr) 1720 (br, s), 1500 (m), 1480 (m), 1220 (s), 1130 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.98 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.15 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.72–3.00 (m, 5 H), 3.12–3.25 (m, 1 H), 3.42–3.50 (m, 1 H), 7.15–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 37.15 (d), 40.95 (t), 43.88 (d), 44.32 (d), 45.20 (d), 51.43 (d), 55.26 (d), 55.49 (d), 56.51 (s), 126.90 (d), 127.25 (d), 128.49 (d), 136.38 (s), 210.60 (s), 211.89 (s); mass spectrum (70 eV), *m/e* (relative intensity) 250 (molecular ion, 100.0), 194 (38.9), 128 (35.4). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.34; H, 5.80.

Reaction of 4 with EDA–F_3B·OEt_2. Diketone **4** (0.74 g, 2.96 mmol) was dissolved in anhydrous methylene chloride (50 mL), and the resulting solution was cooled to 0 °C by application of an external ice bath. Boron trifluoride etherate (0.8 mL, 6 mmol) was added slowly to this cold solution during 5 min with stirring. After all of the Lewis acid had been added, EDA (0.68 g, 5.9 mmol) was added dropwise to the stirred reaction mixture. After all of the EDA had been added, the stirred reaction mixture was allowed to warm gradually to room temperature. The reaction mixture was stirred at room temperature for 2 h. The reaction was then quenched by addition of saturated aqueous sodium bicarbonate

(12) Marchand, A. P.; Suri, S. C.; Earlywine, A. D.; Powell, D. R.; van der Helm, D. *J. Org. Chem.* **1984**, *49*, 670.

(13) Bergmann, E.; Bergmann, F. *J. Org. Chem.* **1938**, *3*, 125.

solution (40 mL). The methylene chloride layer was separated and washed sequentially with water (25 mL) and with brine (25 mL). The remainder of the workup was performed as described above for the corresponding reaction of **3** with EDA–F_3B·OEt_2. Column chromatographic purification of the product (1.1 g) afforded pure **6** (0.25 g, 25%) as a colorless microcrystalline solid: mp 106 °C; IR (KBr) 1720 (br, s), 1650 (br, s), 1610 (br, s), 1410 (s), 1320 (m), 1270 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.2 Hz, 3 H), 1.61 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.81 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.20 (br s, 1 H), 2.80–3.00 (m, 3 H), 3.21 (m, 1 H), 3.45 (d, J = 10.2 Hz, 1 H), 3.61 (m, 1 H), 4.15 (q, J = 7.2 Hz, 2 H), 7.20–7.42 (m, 5 H), 11.98 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.81 (q), 34.48 (d), 37.20 (t), 40.30 (d), 41.55 (d), 43.64 (d), 43.72 (d), 44.73 (d), 55.38 (d), 60.26 (t), 62.28 (s), 99.96 (s), 126.26 (d), 126.39 (d), 127.86 (d), 138.79 (s), 170.19 (s), 173.15 (s), 213.42 (s); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 264 (100.0), 171 (21.4), 158 (21.4), 133 (19.1), 132 (26.7). Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.98; H, 6.14.

Continued elution of the chromatography column afforded a mixture of products (0.36 g), which resisted further attempts at separation and purification. The mixture of products thereby obtained was not characterized.

2-(4′-Cyanophenyl)-*p*-benzoquinone (7). The procedure described by Kvalnes[14] was employed for the synthesis of **7**. Thus, *p*-aminobenzonitrile (25.25 g, 214 mmol) was dissolved in concentrated aqueous hydrochloric acid (60 mL), and the resulting solution was diluted with water (200 mL). This solution was cooled to 0 °C via application of an external ice bath, and a solution of sodium nitrite (20.0 g, 290 mmol) in water (200 mL) was added. Excess nitrous acid thereby produced was destroyed via addition of urea (ca. 3 g). To the resulting clear solution was added sodium acetate (ca. 10 g, excess), and the solution was then added slowly to a solution of *p*-benzoquinone (25.38 g, 280 mmol) in 95% aqueous ethanol (500 mL) with vigorous stirring. The temperature of the reaction mixture was maintained below 25 °C throughout the time of reaction. Stirring was continued for 45 min after the addition of the *p*-cyanobenzenediazonium chloride solution had been completed. During this time, nitrogen was evolved, and the product arylquinone, **7**, slowly precipitated from solution. At the conclusion of the reaction, the product (35.0 g, 94.5%) was isolated via suction filtration. Pure **7** was obtained via recrystallization from benzene as a yellow-orange microcrystalline solid: mp 210–211 °C; IR (KBr) 2215 (m), 1640 (s), 1590 (m), 1335 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 7.76 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.61 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.92 (s, 2 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 103.07 (s), 114.97 (s), 129.93 (d), 132.21 (d), 133.90 (d), 136.56 (s), 137.02 (s), 152.11 (d), 153.31 (d), 194.31 (s), 198.62 (s). Anal. Calcd for $C_{13}H_7NO_2$: C, 74.64; H, 3.37. Found: C, 74.33; H, 3.57.

6-(4′-Cyanophenyl)-1,4α,4aα,5α,8β,8aα-hexahydro-1,4-methanonaphthalene-5,8-dione (8). A mixture of **7** (5.00 g, 23.9 mmol), cyclopentadiene (1.58 g, 24.0 mmol), and benzene (20 mL) was placed in a glass bomb. The bomb was sealed with a screw cap, and the reaction mixture was heated at 80 °C for 2 h. The bomb was opened, and the contents were concentrated in vacuo. The residue was recrystallized from benzene–hexane mixed solvent, thereby affording the corresponding endo Diels–Alder adduct (**8**, 6.0 g, 92%) as a pale yellow microcrystalline solid: mp 142–143 °C; IR (KBr) 2220 (s), 1650 (br, s), 1590 (w), 1400 (m), 1320 (m), 1250 (s), 1120 cm^{-1} (s); UV ($CHCl_3$) λ_{max} (ϵ) 241.2 (11 959), 288.7 nm (10 648); ^{1}H NMR δ 1.45 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.60 (*AB*, J_{AB} = 10.2 Hz, 1 H), 3.25–3.46 (m, 2 H), 3.8 (br s, 2 H), 6.15 (s, 2 H), 6.65 (s, 1 H), 7.42 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.63 (*AB*, J_{AB} = 10.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 48.94 (d), 49.04 (t), 49.36 (d), 49.37 (d), 49.49 (d), 113.47 (s), 118.18 (s), 129.61 (d), 131.99 (d), 135.09 (d), 135.83 (d), 137.80 (s), 139.78 (d), 149.62 (s), 197.67 (s), 198.82 (s); mass spectrum (70 eV), m/e (relative intensity) 275 (molecular ion, 100.0), 248 (15.5), 247 (82.8), 219 (54.0). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.89; H, 4.65.

1-(4′-Cyanophenyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (9). A solution of **8** (6.00 g, 21.3 mmol) in acetone (500 mL) was purged with nitrogen and then was irradiated under nitrogen for 8 h with a 450-W Hanovia medium-pressure mercury lamp (Pyrex filter). At the conclusion of the photolysis, the reaction mixture was concentrated, and the residue was recrystallized from ethyl acetate. Pure **9** (5.8 g, 98%) was thereby obtained as a colorless microcrystalline solid: mp 157–158 °C; IR (KBr) 2220 (s), 1700 (br, s), 1600 (w), 1500 (w), 1410 (m), 1320 (s), 1120 (s), 1090 cm^{-1} (s); ^{1}H NMR (DMSO-d_6) δ 1.55 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.85 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.42–2.48 (m, 1 H), 2.60–2.71 (m, 2 H), 2.72–2.81 (m, 2 H), 2.91–2.95 (m, 1 H), 2.97–3.01 (m, 1 H), 7.45 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.75 (*AB*, J_{AB} = 10.2 Hz, 2 H); ^{13}C NMR (DMSO-d_6) δ 43.52 (d), 43.86 (d), 45.26 (d), 46.01 (d), 50.52 (d), 50.82 (t), 54.01 (d), 56.42 (d), 59.29 (s), 108.80 (s), 118.94 (s), 128.52 (d), 131.58 (d), 145.59 (s), 210.00 (s), 212.58 (s); mass spectrum (70 eV), m/e (relative intensity) 275 (molecular ion, 100.0), 248 (14.2), 247 (76.8), 219 (47.6). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.68; H, 4.80.

Reaction of 9 with EDA–F_3B·OEt_2. Diketone **9** (1.0 g, 3.6 mmol) was dissolved in anhydrous ether (300 mL), and the resulting solution was cooled to −20 °C via application of an external cold bath. Boron trifluoride etherate (0.44 mL, 3.6 mmol) was added slowly to this cold solution during 5 min with stirring. After all of the Lewis acid had been added, EDA (0.41 g, 3.6 mmol) was added dropwise to the stirred reaction mixture. The resulting mixture was stirred at −20 °C for 4 h. The cold bath was then removed, and the reaction mixture was allowed to warm slowly to room temperature. The reaction was quenched via addition of 10% aqueous sodium bicarbonate solution (50 mL). Workup was performed as described above for the corresponding reaction of **3** with EDA–F_3B·OEt_2. Column chromatographic purification of the product afforded pure **10** (0.50 g, 61%) as a colorless microcrystalline solid: mp 174 °C; IR (KBr) 2220 (s), 1720 (br, s), 1600 (br, s), 1410 (m), 1320 (m), 1200 (w), 1070 (m), 1010 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3 H), 1.65 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.90 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.25 (br s, 1 H), 2.80–2.85 (m, 1 H), 2.90–3.02 (m, 2 H), 3.21–3.35 (m, 1 H), 3.45 (d, J = 10.2 Hz, 1 H), 4.60–4.75 (m, 1 H), 4.22 (q, J = 7.2 Hz, 2 H), 7.25 (*AB*, J_{AB} = 7.2 Hz, 2 H), 7.65 (*AB*, J_{AB} = 7.2 Hz, 2 H), 11.80 (br s, 1 H): ^{13}C NMR ($CDCl_3$) δ 14.21 (q), 35.11 (d), 37.68 (t), 40.68 (d), 42.04 (d), 44.02 (d), 44.18 (d), 45.03 (d), 55.67 (d), 60.89 (t), 62.79 (s), 100.69 (s), 110.73 (s), 118.86 (s), 127.59 (d), 132.14 (d), 144.53 (s), 170.44 (s), 172.57 (s), 212.74 (s); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 290 (24.6), 289 (100), 196 (16.2), 183 (15.6), 133 (29.9), 132 (27.5), 127 (13.8), 107 (84.4). Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.13; H, 5.26. Found: C, 73.30; H, 5.31.

6-(4′-Methoxyphenyl)-1,4α,4aα,5α,8β,8aα-hexahydro-1,4-methanonaphthalene-5,8-dione (12). A mixture of 2-(4′-methoxyphenyl)-*p*-benzoquinone[14] (**11**, 4.28 g, 20 mmol), cyclopentadiene (1.32 g, 20 mmol), and benzene (20 mL) was placed in a glass bomb. The bomb was sealed with a screw cap, and the reaction mixture was heated at 80 °C for 2 h. The bomb was opened, and the contents were concentrated in vacuo. The residue was recrystallized from benzene–hexane mixed solvent, thereby affording the corresponding endo Diels–Alder adduct (**12**, 4.0 g, 71%) as a pale yellow microcrystalline solid: mp 105.5–106.5 °C; IR (KBr) 1635 (s), 1585 (s), 1510 (m), 1265 (m), 1235 (s), 1185 cm^{-1} (s); UV ($CHCl_3$) λ_{max} (ϵ) 242.4 (13 388), 346.8 nm (8015); ^{1}H NMR ($CDCl_3$) δ 1.45 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.55 (*AB*, J_{AB} = 10.2 Hz, 1 H), 3.30 (doubled *AB*, J_{AB} = 8.7 Hz, additional coupling J' = 4.2 Hz, 1 H), 3.38 (doubled *AB*, J_{AB} = 8.7 Hz, additional coupling J' = 4.2 Hz, 1 H), 3.55 (br d, 2 H), 3.80 (s, 3 H), 6.10 (s, 2 H), 6.65 (s, 1 H), 6.90 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.40 (*AB*, J_{AB} = 10.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 48.67 (d), 48.91 (t), 49.12 (d), 49.25 (d), 49.66 (d), 55.33 (q), 113.92 (d), 125.43 (s), 130.54 (d), 135.10 (d), 135.64 (d), 137.09 (d), 150.76 (s), 161.29 (s), 198.89 (s), 199.41 (s); mass spectrum (70 eV), m/e (relative intensity) 280 (molecular ion, 100.0), 224 (11.1). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71. Found: C, 77.38; H, 5.95.

1-(4′-Methoxyphenyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (13). A solution of **12** (4.0 g, 28 mmol) in acetone (500 mL) was purged with nitrogen and then was irradiated under nitrogen for 8 h with a 450-W Hanovia medium-pressure mercury lamp (Pyrex filter). At the conclusion of the photolysis, the reaction mixture was concentrated, and the residue was recrystallized from ethyl acetate. Pure **13** (3.7 g, 93%) was thereby obtained as a pale yellow microcrystalline solid: mp 125–126 °C: IR (KBr) 1710 (s), 1600 (s), 1505 (s), 1465 (w), 1435 (w), 1285 (m),

(14) Kvalnes, D. E. *J. Am. Chem. Soc.* **1934**, *56*, 2478.

1240 (s), 1075 (s), 1030 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.99 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.75 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.84–2.85 (m, 1 H), 2.85–2.86 (m, 2 H), 2.87–2.93 (m, 2 H), 2.95–2.96 (m, 1 H), 2.97–2.99 (m, 1 H), 3.02 (s, 3 H), 6.88 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.10 (*AB*, J_{AB} = 10.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.00 (d), 40.89 (t), 43.81 (d), 44.32 (d), 45.06 (d), 51.53 (d), 55.18 (d), 55.20 (d), 55.29 (q), 55.90 (s), 113.96 (d), 128.00 (d), 128.36 (s), 158.73 (s), 210.87 (s), 211.80 (s); mass spectrum (70 eV), *m/e* (relative intensity) 280 (molecular ion, 20.4), 186 (14.4), 132 (15.0). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71. Found: C, 77.03; H, 5.88.

Reaction of 13 with EDA–F_3B·OEt_2. Diketone **13** (300 mg, 1.07 mmol) was dissolved in anhydrous ether (300 mL), and the resulting solution was cooled to −78 °C via application of an external cold bath. Boron trifluoride etherate (0.14 mL, 1.1 mmol) was added slowly to this cold solution during 1 min with stirring. After all of the Lewis acid had been added, EDA (122 mg, 1.08 mmol) was added dropwise to the stirred reaction mixture. The temperature of the reaction was raised to −20 °C, and the resulting mixture was stirred at this temperature for 4 h. The cold bath was then removed, and the reaction mixture was allowed to warm slowly to room temperature. The reaction was quenched via addition of 10% aqueous sodium bicarbonate solution (25 mL). Workup was performed as described above for the corresponding reaction of **3** with EDA–F_3B·OEt_2. Column chromatographic purification of the product afforded pure **14** (148 mg, 37%) as a colorless microcrystalline solid: mp 99–100 °C; IR (KBr) 1720 (s), 1625 (s), 1600 (s), 1510 (m), 1455 (m), 1405 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3 H), 1.68 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.90 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.22 (br s, 1 H), 2.80–3.00 (m, 3 H), 3.19–3.21 (m, 1 H), 3.51 (d, J = 10.2 Hz, 1 H), 3.55–3.65 (m, 1 H), 3.90 (s, 3 H), 4.21 (q, J = 7.2 Hz, 2 H), 6.95 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.18 (*AB*, J_{AB} = 10.2 Hz, 2 H), 11.80 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.22 (q), 34.82 (d), 37.64 (t), 40.75 (d), 41.99 (d), 44.04 (d), 44.20 (d), 45.05 (d), 55.29 (d), 55.73 (q), 60.69 (t), 62.12 (s), 100.34 (s), 113.91 (d), 127.74 (d), 131.12 (s), 158.54 (s), 170.58 (s), 173.50 (s), 214.37 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 295 (20.3), 294 (100.0), 201 (128.6), 132 (11.7). Anal. Calcd for $C_{22}H_{22}O_5$: C, 72.13; H, 6.01. Found: C, 72.36; H, 6.17.

7-(4′-Methoxyphenyl)pentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane-2,6-dione (15). The procedure of Krapcho and co-workers[7b] was utilized to decarboxylate **14**. Thus, a mixture of **14** (200 mg, 0.550 mmol), sodium chloride (16 mg, 0.27 mmol), dimethyl sulfoxide (DMSO, 2 mL), and water (50 mg) was refluxed at 150 °C under nitrogen for 4 h. The reaction mixture was then poured into ice–water, and the resulting mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with water (5 × 10 mL) to remove excess DMSO. The resulting dichloromethane solution was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording crude diketone **15** (130 mg, 81%). Recrystallization of this material from acetone–hexane mixed solvent afforded pure **15** as a colorless microcrystalline solid: mp 164–165 °C; IR (KBr) 1710 (s), 1665 (s), 1505 (m), 1235 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.85 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.07 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.45–2.73 (m, 4 H), 2.81–3.15 (m, 3 H), 3.30–3.45 (m, 2 H), 3.80 (s, 3 H), 6.88 (*AB*, J_{AB} = 10.2 Hz, 2 H), 7.05 (*AB*, J_{AB} = 10.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.98 (d), 38.59 (t), 38.86 (d), 39.50 (t), 41.61 (d), 44.67 (d), 46.69 (d), 51.69 (d), 53.94 (d), 55.38 (q), 58.50 (s), 113.92 (d), 127.48 (d), 131.90 (s), 158.46 (s), 214.15 (s), 219.0 (s); mass spectrum (70 eV), *m/e* (relative intensity) 294 (molecular ion, 100), 201 (79), 133 (63). Anal. Calcd for $C_{19}H_{18}O_3$: M_r 294.1256. Found (high-resolution mass spectrometry): M_r 294.1258.

Reaction of 1 with EDA–F_3B·OEt_2. Cage dione **1**[15] (5.22 g, 30 mmol) was suspended in anhydrous ether (200 mL) and cooled to 0 °C by application of an external ice bath. Boron trifluoride etherate (4.26 g, 30 mmol) was then added slowly with stirring during 5 min. After all of the boron trifluoride etherate had been added, ethyl diazoacetate (4.56 g, 40 mmol) was then added slowly at such a rate that nitrogen was evolved at a slow, steady rate. The reacting mixture was stirred for 2 h after the addition of ethyl diazoacetate had been completed. The reaction mixture was allowed to warm slowly to room temperature and then stirred at room temperature for 2 h. The reaction mixture was then cooled (ice bath), and the reaction was quenched via the addition of saturated aqueous sodium bicarbonate solution (150 mL). The ether layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 150 mL). The combined organic layers were dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording a viscous yellow oil. This oil was purified via column chromatography (silica gel stationary phase). Elution with 10% ethyl acetate–hexane mixed solvent afforded **2** (320 mg, 3%), mp 113–114 °C (lit.[3] mp 108.5–109.0 °C). The infrared, proton NMR, and carbon-13 NMR of the material thereby obtained were consistent with the corresponding spectra of authentic **2**.[3]

Further elution of the chromatography column with 12% ethyl acetate–hexane mixed solvent afforded ethyl 3,6-dioxopentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane-2-carboxylate (**16a**, 1.64 g, 21%) as a colorless microcrystalline solid: mp 95–97 °C; IR (KBr) 1730 (s), 1645 (br, vs), 1420 (m), 1380 (br), 1220 (m), 1190 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.60 (t, J = 7.2 Hz, 3 H), 1.75 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.94 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.15 (s, 1 H), 2.55–3.00 (m, 5 H), 3.31–3.78 (m, 2 H), 4.45 (q, J = 7.2 Hz, 2 H), 11.94 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.18 (q), 35.77 (d), 37.20 (d), 37.72 (d), 38.63 (t), 41.04 (d), 41.88 (d), 45.27 (d), 49.69 (d), 54.76 (d), 60.55 (t), 100.22 (s), 170.51 (s), 173.57 (s), 216.39 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 188 (94.1), 107 (100.0). Anal. Calcd for $C_{15}H_{16}O_4$: M_r 260.1046. Found (high-resolution mass spectrometry): M_r 260.1043.

Finally, elution of the chromatography column with 45% ethyl acetate–hexane mixed solvent afforded ethyl 4,10-dioxotetracyclo[6.4.0.0^{2,6}.0^{5,9}]dodec-11-ene-11-carboxylate (**19**, 1.3 g, 17%) as a colorless microcrystalline solid: mp 126.5–127.0 °C, along with at least two other products (1.2 g) that were not identified. Spectral and microanalytical data for **19**: IR (KBr) 1720 (br, vs), 1660 (s), 1605 (m), 1380 (s), 1270 (br, s), 1150 (s), 1055 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3 H), 1.72 (*AB*, J_{AB} = 10.0 Hz, 1 H), 1.94 (*AB*, J_{AB} = 10.0 Hz, 1 H), 2.18 (br s, 2 H), 2.90 (m, 6 H), 4.21 (q, J = 7.0 Hz, 2 H), 7.51 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.60 (q), 36.94 (t), 37.59 (d), 39.29 (d), 41.23 (t), 45.98 (d), 49.23 (d), 52.94 (d), 53.91 (d), 60.42 (t), 130.65 (s), 156.21 (d), 163.04 (s), 192.88 (s), 216.88 (s); mass spectrum (70 eV), *m/e* (relative intensity) 260 (molecular ion, 36.7), 216 (16.7), 215 (96.7), 188 (100.0), 166 (13.3), 115 (100.0). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.10; H, 6.24.

Pentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane-2,6-dione (17). The procedure of Krapcho and co-workers[7b] was utilized to decarboxylate **16a**. Thus, a mixture of **16a** (460 mg, 1.78 mmol), sodium chloride (150 mg, 2.58 mmol), DMSO (10 mL), and water (ca. 0.5 mL) was refluxed at 165 °C under nitrogen for 4 h. The reaction mixture was then poured into ice–water, and the resulting mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with water (5 × 10 mL) to remove excess DMSO. The resulting dichloromethane solution was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording crude diketone **17** (265 mg, 79%). Recrystallization of this material from acetone–hexane mixed solvent afforded pure **17** as a colorless microcrystalline solid: mp 233–234 °C; IR (KBr) 1720 (m), 1700 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.60 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.88 (*AB*, J_{AB} = 10.2 Hz, 1 H), 2.18 (br s, 2 H), 2.31–3.33 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 38.10 (d), 38.73 (t), 39.12 (d), 39.19 (t), 40.20 (d), 41.64 (d), 43.64 (d), 35.79 (d), 46.37 (d), 53.17 (d), 209.33 (s), 217.98 (s); mass spectrum (70 eV) *m/e* (relative intensity) 188 (molecular ion, 98.3), 160 (31.4). Anal. Calcd for $C_{12}H_{12}O_2$: M_r 188.0837. Found (high-resolution mass spectrometry): M_r 188.0834.

Base-Promoted Friedlaender Condensation of 17 with *o*-Aminobenzaldehyde. To a mixture of cage diketone **17** (100 mg, 0.53 mmol) and *o*-aminobenzaldehyde (64 mg, 0.53 mmol) in absolute ethanol (5 mL) was added a solution of potassium hydroxide (25 mg, excess) in absolute ethanol (2 mL). The resulting mixture was refluxed under nitrogen for 6 h. The reaction mixture was then allowed to cool to room temperature. Water (5 mL) was added, and the resulting mixture was extracted with methylene chloride. The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording crude **18** (105 mg, 73%). The crude

(15) Marchand, A. P.; Allen, R. W. *J. Org. Chem.* **1974**, *39*, 1596.

product was purified via recrystallization from ethyl acetate. Pure **18** was thereby obtained as a colorless microcrystalline solid: mp 195–196 °C; IR (KBr) 1710 (s), 1600 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.71 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.0 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.05 (s, 1 H), 2.24 (s, 1 H), 3.0 (br s, 4 H), 3.36–3.57 (m, 1 H), 4.12 (br s, 1 H), 7.15–8.1 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 37.91 (d), 38.30 (d), 38.89 (d), 39.21 (t), 40.97 (d), 45.52 (d), 48.97 (d), 50.07 (d), 55.93 (d), 125.90 (d), 127.13 (d), 127.59 (s), 128.76 (2 C, d), 131.82 (s), 134.29 (d), 147.03 (s), 158.61 (s), 216.62 (s). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.52; H, 5.49. Found: C, 83.21; H, 5.64.

X-ray Crystallographic Analyses of 5, 6, 10, 15, and 18. All X-ray data were collected on a Nicolet R3m/μ update of a $P2_1$ diffractometer with use of the Wyckoff mode (2θ fixed, ω varied), with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A ψ-scan empirical absorption correction was applied to all data. The structures were solved by direct methods and refined by block-cascade anisotropic least-squares techniques. Hydrogen atom positional parameters were refined, except for the ethyl hydrogen atoms in the CO_2Et group of **5**, by using a single refined isotropic thermal parameter. All computer programs were used as supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configurations. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters for **5, 6, 10, 15,** and **18**; selected bond distances and valence angles for **5, 6,** and **10**; structure drawings for compounds **5, 6, 10, 15,** and **18** (37 pages); observed and calculated structure factors for **5, 6, 10, 15,** and **18** (63 pages). Ordering information is given on any current masthead page.

Reactions with Aziridines. 48.[1] Friedel–Crafts Reactions with N-Sulfonated Aziridines and with Open-Chain Sulfonamides. Sulfonamides as Leaving Groups in Open-Chain Structures

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$AlCl_3$-catalyzed reactions of *N*-sulfonylaziridines (C substituents given) **1a** (no substituent), **4b** (2-phenyl), **8b** (2,3-diphenyl), and **11a–c** (2,2-dimethyl) with neat benzene, toluene, or anisole proceeded rapidly without heating. The expected *N*-sulfonyl(arylethyl)amines **2, 5, 9,** and **12** were obtained in yields of 0–84%. Apart from **1a**, the main byproducts (or the main products) **6, 10, 13,** and **14** had incorporated two molecules of arene under elimination of the corresponding isolable sulfonamides **7**. The two arene molecules were attached to both carbon atoms of the original aziridine ring, except in the reaction with **11**, where 2,3-diarylation (forming **13**) was accompanied or even replaced by 3,3-diarylation (forming **14**). Open-chain sulfonamides behave analogously provided their structure allows easy formation of a carbenium ion intermediate. Mechanisms for the formation of the non-sulfonamide products **6, 10, 13,** and **14** are proposed. Some results point to an equilibrium between a benzyl and a tertiary alkyl cation.

The high reactivity of activated aziridines[2] toward nucleophiles can be enormously increased by acid catalysis (double activation[3]) as is well known for oxiranes from the classic work of Brønsted, Kilpatrick, and Kilpatrick.[4]

When the two ring carbons of an activated aziridine carry different substituents, the regioselectivity of ring opening usually depends on the absence or presence of a catalytically effective acid. It usually changes then in a manner that is compatible with a change from S_N2 to S_N1.[2,3,5] It was shown, however, that in alcoholyses[3,6] and in reactions with Grignard reagents[5] (halide attack following a coordination of a Mg^{2+} species to the activated aziridine) a borderline mechanism without occurrence of a carbenium ion prevails.

Only few Friedel–Crafts reactions with activated aziridines have been reported so far.[7,8] A carbenium intermediate has been postulated that in one case has been proven through a rearrangement.[7] The reason for the very limited number[9] of reported reactions may be related to the low yields of isolated material, which only once (guaiazulene, BF_3 as catalyst)[8] exceeded 50%. Reasons for low yields of the desired products (derivatives of (2-arylethyl)amines) as well as further evidence for carbenium

(1) Part 47: Stamm, H.; Speth, D. *Arch. Pharm. (Weinheim)* in the press. Part 46: Mall, T.; Stamm, H. *Chem. Ber.* **1988**, *121*, 1353–1355.
(2) Ham, G. E. *J. Org. Chem.* **1964**, *29*, 3052–3055.
(3) Buchholz, B.; Stamm, H. *Isr. J. Chem.* **1986**, *27*, 17–23.
(4) Cited together with more recent papers in the following: Biggs, J.; Chapman, N. B.; Finch, A. F.; Wray, V. *J. Chem. Soc. B* **1971**, 55–63.
(5) Onistschenko, A.; Buchholz, B.; Stamm, H. *Tetrahedron* **1987**, *43*, 565–576.
(6) Compare also: Takeuchi, H.; Koyama, K. *J. Chem. Soc., Perkin Trans. 2* **1981**, 121–126. However, some results are difficult to explain by the proposed mechanism, and the kinetic evidence (second order in $MeCO_2H$) can perhaps be related with a dimerization of $MeCO_2H$ in cyclohexane. Activation by the weak acid $MeCO_2H$ needs further corroboration.
(7) Genssler, W. J.; Rockett, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 3262–3264. Genssler, W. J.; Kohler, W. R. *J. Org. Chem.* **1962**, *27*, 2754–2762. Genssler, W. J.; Dheer, S. K. *J. Org. Chem.* **1981**, *46*, 4051–4057.
(8) Kurokawa, S.; Anderson, A. G., Jr. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2059–2064.
(9) It is noteworthy that in a recent chapter[10] on Friedel–Crafts alkylation the usefulness of ethylene oxide and cyclopropane is stated without mentioning the aziridines.

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