Electrocyclization Rates for Some Donor-Acceptor-Substituted Trienes

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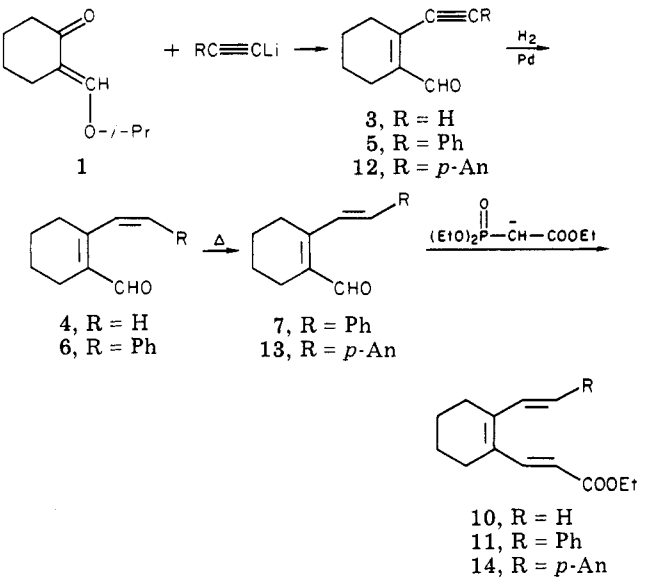
Three new trienes, ethyl 3-(2-vinylcyclohexenyl)-*trans*-propenoate (**10**), ethyl 3-(2-*trans*-styrylcyclohexenyl)-*trans*-propenoate (**11**), and ethyl 3-[2-*trans*-(*p*-methoxystyryl)cyclohexenyl]-*trans*-propenoate (**14**), have been prepared and characterized. The kinetics of the thermal electrocyclization of each was determined in an inert solvent. The results were as follows: **10**, k(137 °C) = 1.03 × 10^{-4} s^{-1}, $\Delta H^{\ddagger}$ = 109.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −58.6 J mol^{-} K^{-1}; **11**, k(137 °C) = 4.03 × 10^{-4} s^{-1}, $\Delta H^{\ddagger}$ = 113.0 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −37.7 J mol^{-1} K^{-1}; **14**, k(137 °C) = 4.03 × 10^{-4} s^{-1}, $\Delta H^{\ddagger}$ = 113.0 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −37.7 J mol^{-1} K^{-1}. Compared to 1,2-divinylcyclohexene as a standard **10** has a relative rate of 1.0, and **11** and **14** have relative rates of 4.0. Clearly these triene cyclization rates are virtually independent of the donor/acceptor properties of the substituents.

The general theoretical treatments of pericyclic reactions lead to the division of these reactions into allowed and forbidden classes, but they do not treat the influence of substitution or the possibility that substitution could alter the predictions of the theory. In an interesting series of papers, Epiotis provided a theoretical treatment of the possible influence of substitution on a variety of pericyclic reactions.[1,2] In accord with other researchers,[3] Epiotis concluded that configuration interaction would play a dominant role in facilitating forbidden pericyclic reactions. Epiotis went on to show that what he called "push–pull" substituion, i.e., an unsymmetrical array of donor–acceptor substituents, should prove most efficacious in enhancing configuration interaction. Finally, he suggested that for electrocyclic reactions such substitution would lower the stabilization energy for the transition state of the allowed process. Since we had had a continuing interest in the effect of substituents on the triene–cyclodiene electrocyclic process, we decided to test Epiotis' theory as it applies in this case.

In the case of triene electrocyclization, the most effective substitutions would be on the terminal atoms of the triene. It has been shown that such substituents in a trans position have little steric interaction, but in a cis arrangement, their steric effects dominate. Since the Epiotis theory relates to electronic factors, we chose to begin our studies with substituents trans on terminal positions only. All trienes were prepared by a procedure developed by Schiess and co-workers (Scheme I).[4,5] The process is convenient since it places the central double bond in a cyclohexane ring, obviating the usual problems of preparing a central cis double bond. Overall, the scheme gives good yields and permits control of the stereochemistry of both terminal double bonds.

Introduction of the first double bond in the Schiess procedure is accomplished in two steps, an advantage if the cis stereoisomer is desired but perhaps unnecessary if only the trans form is needed. The pioneering study of Drieding and Nickel[6] showed that alkyl Grignard reagents tended toward 1,4-addition to 1 and that alkyllithium reagents gave mixtures. However, no thorough study of the use of unsaturated organometallics with 1 appears to have been made. As a part of our work on this reaction

Scheme I



we found that etherification of 2-(hydroxymethylene)-cyclohexanone with isopropyl bromide gives mainly **1**, but about 15% of 2-isopropoxy-3,4,5,6-tetrahydrobenzaldehyde (**2**) is also formed. Treatment of pure **1** with vinyllithium gives **4** directly in reasonable yield. On the other hand, vinylmagnesium bromide gives predominantly 2-(2-propenylidene)-1-vinylcyclohexanol (**8**) via a sequential 1,4- and 1,2-addition process. It is particularly interesting that propynylmagnesium bromide adds twice in a similar pattern to produce 3-(2-butynylidene)-2-(1-propynyl)-cyclohexene (**9**), a rare example of 1,4-addition by an acetylenic Grignard reagent.

All three trienes **10**, **11**, and **14** undergo thermal cyclization in inert solvents at temperatures in the 120–150 °C range. In all of our studies of divinylcyclohexenes, ring closure leads initially to the expected homoannular diene, but further heating generally gives a product with a typical *s*-trans diene ultraviolet spectrum.[7] Both **11** and **14** give isolable amounts of the expected homoannular dienes which appear to be single isomers. Conversely, **10** did not provide an isolable homoannular diene but gave predominantly a rearranged diene (eq 1). This product, which may contain small amounts of other isomers, was assigned the structure of 2-carbethoxy-1,2,3,5,6,7-hexahydronaphthalene (**15**) on the basis of spectral information. The

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(3) See for example: Baldwin, J. E. "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds; Academic Press: New York, 1977; Vol. II, pp 272–302.
(4) Schiess, P.; Chia, H. L. *Helv. Chim. Acta* **1970**, *53*, 485.
(5) Schiess, P.; Seeger, R.; Suter, C. *Helv. Chim. Acta* **1970**, 53, 1713.
(6) Drieding, A. S.; Nickel, S. *J. Am. Chem. Soc.* **1954**, *76*, 3965.
(7) Marvell, E. N.; Caple, G.; Delphey, C.; Platt, J.; Polston, N.; Tashiro, J., *Tetrahedron* **1973**, *29*, 3797.

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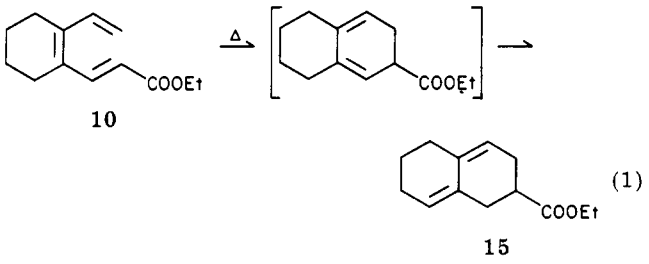

10 15 (1)

ultraviolet spectrum [241 nm (ε 14 000)], and the presence of only two olefinic protons in its NMR spectrum permit only two possible structures. Absence of any peak in the 3.4–3.8-ppm region argues against the presence of a β,γ-unsaturated ester unit, leaving **15** as the only reasonable structure. No reasons why this compound is the main product or why the diene rearrangement is so facile can be given.

Kinetics of the ring-closure reactions of **10**, **11**, and **14** were followed by the disappearance of the ultraviolet band of the reactant. Rates were followed to at least 2 half-lives and showed good first-order rate constants. Reactions were run in either cyclohexane or methylcyclohexane at several temperatures (Table I). It is interesting that these rates are subject to only minor variation with substitution. Compared with divinylcyclohexene (3.7×10^{-5} s^{-1} at 126.5 °C),[7] **10** has a relative rate of 1.0, while at 137 °C both **11** and **14** have the same relative rate of 4.0. The results thus indicate that push–pull substitution has very little effect on rates of triene electrocyclization when the substituents are in a trans position on terminal atoms. Also, the trend, small as it is, increases the rate rather than lowering it. The rate reported by Schiess, Seeger, and Suter[5] for *trans,trans*-distyrylcyclohexene (2.3×10^{-3} s^{-1} at 150 °C) supports the very slight sensitivity of the rate to substitution. The activation parameters calculated for the trienes are as follows: **10**, $\Delta H^{\ddagger}$ = 109.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −58.6 J mol^{-1} K^{-1}; **11** and **14** $\Delta H^{\ddagger}$ = 113.0 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −37.7 J mol^{-1} K^{-1}.

We had planned to investigate the stereochemistry of the ring closure of **11** in detail. To accomplish this, we intended to convert **16** to the octalin 2-phenyl-3-carbethoxy-1,2,3,4,5,6,7,8-octahydronaphthalene. Unfortunately, partial hydrogenation over surface-active catalysts led inevitably to a complex mixture, and the use of the homogeneous catalyst recommended for 1,4-hydrogenation[8] gave only aromatization to 2-phenyl-3-carbethoxy-5,6,7,8-tetrahydronaphthalene. The product **16** from the ring closure of **11** appeared to be a single substance. No trace of any compound other than the rearranged diene was noted in attempts to analyze the material via gas chroamtography, and no separation was achieved by thin-layer chromatography. While it was not possible to assign the stereochemistry from the spectral data, we see no reason to assume it was not the expected cis isomer.

Experimental Section

2-(Isopropoxymethylene)cyclohexanone (1) and 2-Isopropoxy-3,4,5,6-tetrahydrobenzaldehyde (2). A modification of the method of Johnson and Posvic[9] was used. Crude 2-(hydroxymethylene)cyclohexanone (63.0 g, 0.500 mol), 40.0 g (0.579 mol) of ignited potassium carbonate, and 73.8 g (0.600 mol) of 2-bromopropane in 200 mL of Me_2SO were stirred and heated at 50 °C for 12 h. The organic material was taken up in ether, and the Me_2SO was washed out with water. The ether solution was dried ($MgSO_4$) and concentrated, and the residue was distilled to give 69.2 g (83%) of a mixture of **1** (ca. 85%) and **2** (ca. 15%). The mixture was separated by distillation on a spinning-band column, which gave **1**: bp 72–73 (0.1 torr) [lit.[9] bp 72–73 °C (0.1 torr)]; NMR (CCl_4) δ 1.29 (d, 6 H, J = 6 Hz), 1.5–1.9 (m, 4 H), 2.1–2.5 (m, 4 H), 4.20 (septet, 1 H, J = 6 Hz), 7.24 (t, 1 H, J = 2.5 Hz); UV max (EtOH) 277 nm (ε 16 900).

A fraction enriched in **2** [bp 76–78 °C (0.1 torr)] was separated by GLC (6 ft × $^1/_4$ in., 5% FFAP on Chromosorb G at 100 °C) to give a pure sample of **2**: NMR (CCl_4) δ 1.25 (d, 6 H, J = 6 Hz), 1.5–1.9 (m, 4 H), 2.1–2.4 (m, 4 H), 4.46 (septet, 1 H, J = 6 Hz), 10.06 (s, 1 H); IR (neat) 3060, 1665, 1615, 1380, 1190, 1160 cm^{-1}; UV max (EtOH) 276 nm (ε 15 500). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.10; H, 9.60.

2-Ethynyl-3,4,5,6-tetrahydrobenzaldehyde (3). This substance was prepared in 0.1-mol quantities by the procedure of Schiess and Chia.[4] The product [mp 49–51 °C (lit.[4] mp 50–52 °C)] was obtained in 51% yield.

2-Vinyl-3,4,5,6-tetrahydrobenzaldehyde (4). Method A. This compound was prepared in 84% yield by hydrogenation of **3** over Lindlar catalyst by following the directions of Schiess and Chia.[4]

Method B. Under nitrogen, 155 mL (0.122 mol) of 0.79 M vinyllithium in THF was added over 30 min to a stirred solution containing 20.5 g (0.122 mol) of **1** in 500 mL of THF. The reaction mixture was stirred 1 h at 0 °C, and it was then treated with saturated NH_4Cl. Ether was added, and the THF was washed out with water. The ether was removed, and the residual material was mixed with 100 mL of EtOH and 100 mL of 2 N H_2SO_4 and allowed to stand 3 h at 25 °C. The organic product was taken up in ether and dried ($MgSO_4$), and the solvent was removed. The residue was distilled: bp 46–48 °C (0.1 torr) [lit.[4] bp 45 °C (0.02 torr)]; 8.46 g (51%); NMR (CCl_4) δ 1.5–1.9 (m, 4 H), 2.2–2.6 (m, 4 H), 5.39 (d, 1 H, J = 11 Hz), 5.48 (d, 1 H, J = 17 Hz), 7.34 (dd, 1 H, J = 11, 17 Hz), 10.26 (s, 1 H).

2-(Phenylethynyl)-3,4,5,6-tetrahydrobenzaldehyde (5). Compound **5** was prepared in 45% yield according to the procedure of Schiess, Seeger, and Suter.[5] The NMR spectrum was in accord with the literature[5] spectrum.

2-(*cis*-β-Styryl)-3,4,5,6-tetrahydrobenzaldehyde (6). Compound **6** was obtained by partial hydrogenation of **5** over Pd/C catalyst according to the directions of Schiess, Seeger, and Suter.[5] The product was not isolated but was used directly in the next reaction.

2-(*trans*-β-Styryl)-3,4,5,6-tetrahydrobenzaldehyde (7). A solution of **6** in methylcyclohexane was heated to boiling under nitrogen for 8 h. The product was recrystallized from cyclohexane: mp 78.5–80.5 °C (lit.[5] mp 80–82); yield 42%; NMR (CCl_4) δ 1.5–1.8 (m, 4 H), 2.1–2.6 (m, 4 H), 6.70 (d, 1 H, J = 17 Hz), 7.1 (m, 5 H), 7.65 (d, 1 H, J = 17 Hz), 10.3 (s, 1 H).

2-(2-Propenylidene)-1-vinylcyclohexanol (8). A solution containing 33.6 g (0.200 mol) of **1** in 50 mL of THF was added under N_2 to a cold (0 °C) solution containing 0.500 mol of vinylmagnesium bromide in 150 mL of THF. The mixture was stirred 10 h at room temperature, and 500 mL of cold 3 N NH_3 saturated with NH_4Cl was added. The organic products were taken up in ether, and the THF was washed out with water. The ether solution was dried ($MgSO_4$), and the ether was removed. The residue was distilled to give **8**: 17.1 g (52%), bp 74–76 °C (0.25 torr); NMR (CCl_4) δ 1.3–1.8 (m, 6 H), 1.98 (s, 1 H, OH),

Table I. Rates of Ring Closure for Trienes 10, 11, and 14

temp, °C	triene rates, 10^5k, s^{-1} 10	11	14
114.6		5.04	5.11
121.1			9.67
122.5		10.9	
124.4		12.5	
127.0	3.91		
130.3	5.77	20.7	22.3
137.0	10.3	40.3	40.3
140.5	15.3		
150.0	23.6		

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(9) Johnson, W. S.; Posvic, H. *J. Am. Chem. Soc.* **1947**, *69*, 1361.

2.0–2.6 (m, 2 H), 4.9–5.4 (m, 4 H), 5.99 (dd, 1 H, J = 11, 18 Hz), 6.01 (d, 1 H, J = 11 Hz), 6.53 (m, 1 H); IR (CCl_4) 3590, 3320, 3100, 1640 cm^{-1}; UV max (cyclohexane) 237 nm (ϵ 22000). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.19; H, 9.66.

1-Ethyl-2-propylcyclohexanol. A sample of **8** (55 mg) was hydrogenated over platinum oxide in cyclohexane. GLC analysis indicated the presence of two isomers with almost equivalent mass spectra. One was shown by GLC to be identical with the major product of the reaction of ethylmagnesium bromide with 2-propylcyclohexanone.

3-(2-Butynylidene)-2-(1-propynyl)cyclohexene (9). A solution containing 6.66 g (0.0396 mol) of **1** in 3/ mL of ether was added under nitrogen to a cold (0 °C) solution containing 0.119 mol of propynylmagnesium bromide in 400 mL of ether. The mixture was heated to reflux for 30 min and was treated with 3 N aqueous ammonia saturated with NH_4Cl. The ether layer was separated and dried ($MgSO_4$). Distillation gave 4.73 g (64%) of 2-(2-butynylidene)-1-(1-propynyl)cyclohexanol as a yellow oil: bp 80–85 °C (0.005 torr); IR (neat) 3570, 3350, 3060, 2225 cm^{-1}; mass spectrum, m/e (relative intensity) 188 (2), 170 (35), 155 (30); UV max (EtOH) 234 nm.

This product dehydrated during attempted purification via GLC (5% Carbowax on Chromosorb W at 170 °C). Compound **9** exhibited the following properties: NMR (CCl_4) δ 1.72 (approx quintet, 2 H, $J \approx 6$ Hz), 1.99 (s, 3 H), 2.03 (d, 3 H, J = 3 Hz), 2.26 (rough q, 2 H, $J \approx 6$ Hz), 2.56 (dt, 2 H, $J \approx 2, 6$ Hz), 5.80 (m, 1 H), 6.11 (t, 1 H, J = 5 Hz); IR (neat) 3080, 2225 cm^{-1}; UV max (EtOH) 272 nm (ϵ 8600). Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 92.06; H, 8.23.

Ethyl 3-(2-Vinyl-1-cyclohexenyl)propenoate (10). A solution containing 2.55 g (11.3 mmol) of triethyl phosphonoacetate in 4 mL of benzene was treated under nitrogen with 0.425 g (10.5 mmol) of sodium hydride. To this was added a solution containing 0.727 g (5.35 mmol) of **4** in 1 mL of benzene, and the solution was heated to 70 °C. The benzene solution was separated from precipitated solids, and the benzene was removed. Distillation gave **10**: 661 mg (60%); bp 87–88 (0.02 torr); NMR (CCl_4) δ 1.27 (t, 3 H, J = 7 Hz), 1.68 (m, 4 H), 2.31 (m, 4 H), 4.16 (q, 2 H, J = 7 Hz), 5.19 (d, 1 H, J = 11 Hz), 5.31 (d, 1 H, J = 17 Hz), 5.73 (d, 1 H, J = 16 Hz), 7.12 (dd, 1 H, J = 11, 17 Hz) 7.93 (d, 1 H, J = 16 Hz); IR (CCl_4) 1720, 1625, 1300 cm^{-1}; UV max (EtOH) 291 nm (ϵ 16400), 299 (22700), 305 (16800). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.45; H, 8.99.

Ethyl 3-(*trans*-2-Styrylcyclohexen-1-yl)-*trans*-propenoate (11). This compound was prepared on a 4.5-mmol scale from **7** according to the procedure for **10**. The benzene solution was chroamtographed over silica with an ether eluant. The eluate was concentrated and rechromatographed with ether/pentane (10/90) as the eluant. The concentrate was crystallized from cyclohexane: mp 46–48 °C; 1.16 g (89%); white crystals; NMR (CCl_4) δ 1.16 (t, 3 H, J = 7 Hz), 1.5–1.9 (m, 4 H), 2.1–2.6 (m, 4 H), 4.18 (q, 2 H, J = 7 Hz), 5.81 (d, 1 H, J = 15 Hz), 6.61 (d, 1 H, J = 15 Hz), 7.1–7.5 (m, 5 H), 7.48 (d, partly overlapping, 1 H, J = 15 Hz), 8.07 (d, 1 H, J = 15 Hz); IR (CCl_4) 1695, 960 cm^{-1}; UV max (cyclohexane) 343 nm (ϵ 54000), 258 (32000). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.66; H, 7.91.

2-[(*p*-Methoxyphenyl)ethenyl]-3,4,5,6-tetrahydrobenzaldehyde (12). A solution containing 14.0 g (0.106 mol) of (*p*-methoxyphenyl)acetylene in 25 mL of ether was added to 60 mL of 1.8 M methyllithium in ether at 0 °C. After the solution had been stirred 2 h at 0 °C, it was cooled to −40 °C, and a solution containing 17.8 g (0.100 mol) of **1** in 60 mL of ether was added. The mixture was stirred at −40 to −50 °C for 15 min and then was allowed to warm to 0 °C. To this was added 210 mL of cold 5% acetic acid. The layers were separated, and the aqueous layer was extracted with ether. The ether solutions were combined, washed with water, and concentrated. The residue was dissolved in 250 mL of isopropyl alcohol, and 150 mL of 1 M sulfuric acid was added. The mixture was stirred 3.5 h, and then 300 mL of water was added. This solution was extracted repeatedly with ether. The ether solution was washed with 1 N sodium hydroxide followed by saturated aqueous sodium chloride and then was dried ($MgSO_4$). Distillation (Kugelrohr) gave 12: 5.2 g (22%); NMR (CCl_4) δ 1.4–1.9 (m, 4 H), 2.0–2.6 (m, 4 H), 3.77 (s, 3 H), 6.84 (d, 2 H, J = 10 Hz), 7.31 (d, 2 H, J = 10 Hz), 10.19 (s, 1 H); IR (CCl_4), 2285, 1675 cm^{-1}; UV max (cyclohexane) 320 nm (ϵ 24000), 259 (16000), 247 (22000).

***trans*-2-(*p*-Methoxystyryl)-3,4,5,6-tetrahydrobenzaldehyde (13).** The alkyne **12** was dissolved in 30 mL of cyclohexane and was hydrogenated over 1.0 g of 10% palladium on charcoal until 1.05 equiv of hydrogen had been taken up. The solution was concentrated, and the residue was dissolved in 50 mL of methylcyclohexane. This solution was heated under reflux for 6.5 h, and then the solvent was distilled. The residual oil was chromatographed over silica gel with ether as eluant. The eluate was concentrated, and the oil was crystallized from ether/methylcyclohexane (1:4) to give **13**: 1.84 g (37%); orange crystals; mp 57–58 °C; NMR (CCl_4) δ 1.5–1.9 (m, 4 H), 2.2–2.6 (m, 4 H), 3.79 (s, 3 H), 6.68 (d, 1 H, J = 16 Hz), 6.75 and 7.36 (AB, 4 H, J = 10 Hz), 7.62 (d, 1 H, J = 16 Hz), 10.52 (s, 1 H); IR (CCl_4) 1695 cm^{-1}; UV max (cyclohexane) 336 nm (ϵ 20000), 256 (11000). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.32; H, 7.50.

Ethyl 3-[*trans*-2-(*p*-Methoxystyryl)cyclohexen-1-yl]-*trans*-propenoate (14). This compound was prepared from **13** by the procedure used to prepare **10**. The reaction was carried out with 1.16 g (4.79 mmol) of **13**, and the resultant benzene solution was chromatographed over silica gel with ether/petroleum ether (15:85) as the eluant. The eluate was concentrated, and the residue was recrystallized at low temperature from methylcyclohexane. The product was obtained as light yellow crystals: mp 66–67 °C; NMR (CCl_4) δ 1.33 (t, 3 H, J = 7 Hz), 1.6–1.9 (m, 4 H), 2.2–2.6 (m, 4 H), 3.80 (s, 3 H), 4.13 (q, 2 H, J = 7 Hz), 5.84 (d, 1 H, J = 16 Hz), 6.60 (d, 1 H, J = 16 Hz), 6.81 and 7.36 (AB, 4 H, J = 10 Hz), 7.38 (d, 1 H, J = 16 Hz), 8.10 (d, 1 H, J = 16 Hz); IR (CCl_4) 1705 cm^{-1}; UV max (cyclohexane) 356 nm (ϵ 33000). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 77.05; H, 7.85.

2-Carbethoxy-1,2,3,5,6,7-hexahydronaphthalene (15). A solution containing 100 mg of **10** in 6 mL of spectral grade cyclohexane was heated at 140 °C for 12 h in a sealed tube. The solvent was removed by distillation, and the residue was chromatographed on activity grade III alumina with cyclohexane as the eluant. Distillation gave 30 mg of a yellow oil: bp 75 °C (0.02 torr); NMR (CCl_4) δ 1.10 (t, 3 H, J = 7 Hz), 1.4–2.0 (m, 4 H), 2.0–2.6 (m, 7 H), 4.08 (q, 2 H, J = 7 Hz), 5.3–5.6 (m, 2 H); IR (CCl_4) 1731 cm^{-1}; UV max (EtOH) 241 nm (ϵ 14000).

6-Carbethoxy-7-phenyl-1,2,3,4,6,7-hexahydronaphthalene (16). A 5% solution of **11** in methylcyclohexane was heated in a sealed tube under nitrogen at 115 °C for 24 h. The solvent was removed to give an oil: NMR (CCl_4) δ 0.98 (t, 3 H, J = 7 Hz), 1.4–1.9 (m, 4 H), 2.1–2.5 (m, 4 H), 3.70 (m, 2 H), 3.86 (q, 2 H, J = 7 Hz), 5.61 (br m, 2 H), 7.10 (s, 5 H); UV max (cyclohexane) 262 nm (ϵ 3400), 273 (sh, 3000). Heating this product at 135–150 °C converted it into an isomeric compound with a UV max (cyclohexane) of 243 nm.

6-Carbethoxy-7-(*p*-methoxyphenyl)-1,2,3,4,6,7-tetrahydronaphthalene (17). A 4% solution of **14** in cyclohexane was heated in a sealed tube under nitrogen at 115 °C for 24 h. Evaporation of the solvent gave an oil: NMR (CCl_4) δ 1.08 (t, 3 H, J = 7 Hz), 1.4–1.9 (m, 4 H), 2.1–2.5 (m, 4 H), 3.67 (br s, 2 H), 3.71 (s, 3 H), 3.93 (q, 2 H, J = 7 Hz), 5.60 (br s, 2 H), 6.66 (d, 2 H, J = 9 Hz), 7.02 (d, 2 H, J = 9 Hz); IR (CCl_4) 1740 cm^{-1}; UV max (cyclohexane) 276 nm (ϵ 2000), 283 (1700).

6-Carbethoxy-7-phenyl-1,2,3,4-tetrahydronaphthalene (18). A solution containing 185 mg (0.67 mmol) in **16** in 2.5 mL of acetone was placed in a high-pressure hydrogenation bomb with 10 mg of (naphthalene)chromium tricarbonyl under 2000 psi of hydrogen. The solution was shaken at room temperature for 24 h. The resulting solution was chromatographed on silica gel, and the eluate was concentrated to give an oil: NMR (CCl_4) δ 0.95 (t, 3 H, J = 7 Hz), 1.8–2.0 (m, 4 H), 2.7–3.0 (m, 4 H), 4.00 (q, 2 H, J = 7 Hz), 7.0 (s, 1 H), 7.15 (m, 5 H), 7.50 (s, 1 H); mass spectrum, m/z (relative intensity) 280 (100), 235 (92).

Acknowledgment. We acknowledge financial aid from the National Science Foundation in the purchase of the NMR instruments used in this research.

Registry No. **1**, 15839-23-3; **2**, 87156-47-6; **3**, 21403-36-1; **4**, 21403-37-2; **5**, 21403-38-3; (*Z*)-**6**, 21451-41-2; (*E*)-**7**, 21451-97-8; **8**, 87156-48-7; **9**, 87156-50-1; (*E*)-**10**, 87156-44-3; (*E,E*)-**11**,

87156-45-4; **12**, 87156-51-2; (*E*)-**13**, 87156-54-5; (*E,E*)-**14**, 87156-46-5; **15**, 87156-55-6; **16**, 87156-56-7; **17**, 87156-52-3; **18**, 87156-53-4; 1,2-divinylcyclohexene, 53081-66-6; 2-(hydroxymethylene)cyclohexanone, 823-45-0; 2-bromopropane, 75-26-3; vinyllithium, 917-57-7; vinyl bromide, 593-60-2; 1-ethyl-2-propyl-1-cyclohexanol, 87156-49-8; ethyl bromide, 74-96-4; 2-propylcyclohexanone, 94-65-5; propynyl bromide, 106-96-7; triethyl phosphonoacetate, 867-13-0; (*p*-methoxyphenyl)acetylene, 768-60-5; methyllithium, 917-54-4; 2-(*p*-methoxyphenyl)ethynyllithium, 52999-18-5; 2-(2-butynylidene)-1-(1-propynyl)cyclohexanol, 87156-57-8.

Benzvalene and Dewar Benzene Type Sulfinamides

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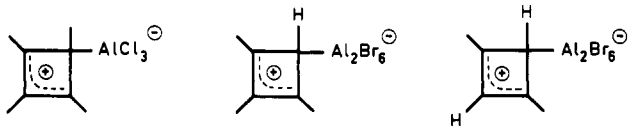
The reaction of cyclobutadiene aluminum halide σ complexes with *N*-arylsulfinylamines leads, depending on the substitution pattern of the phenyl ring, to either bicyclic (Dewar benzene type) or tricyclic sulfinamides, the latter being formed via an intramolecular Friedel–Crafts reaction of an intermediate cyclobutenyl cation. A similar reaction of aluminum halide σ complex **1** with *N*-*tert*-butylsulfinylamine affords both a bicyclic and a tricyclic (benzvalene type) sulfinamide.

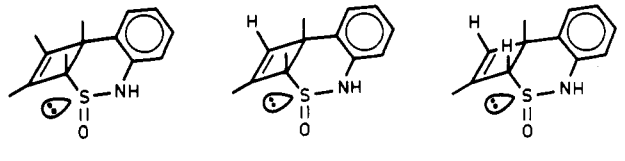
Aluminum halide σ complexes of cyclobutadienes[1] have been known for a decade. These complexes, e.g., **1–3**, are



1 **2** **3**

easily prepared from aluminum halides and alkynes and have proven their synthetic utility in various reactions. Dewar benzenes,[2] bicyclohexenes,[3] Dewar pyridones,[4] pyridines,[5] and a number of other derivatives[6] are obtained upon the reaction of these complexes with appropriate reagents.

Very recently it has been shown that the reaction of **1** with *N*-phenylsulfinylamine[6] at −60 °C leads to sulfinamide **4**. Now we report two novel compound types obtained



4 **5** **6**

in the reaction of the aluminum halide σ complexes of cyclobutadienes with sulfinylamines and, moreover, to point out some of the mechanistic details of the reported reaction by variation of the substituents. Complexes **2** and **3** are very useful in this respect because of their "hydrogen labels". When the reactions of **2** and **3** are performed with *N*-phenylsulfinylamine at −60 °C, only one sulfinamide is isolated (52% and 55% yields, respectively) in each instance. The structural assignments of compounds **5** and **6** are based on a comparison of the ^1H and ^{13}C NMR data with those of sulfinamide **4** and related structures.[7] The regiospecific formation of only one sulfinamide in each case makes a reaction mechanism involving the addition of *N*-phenylsulfinylamine to intermediately formed free tetramethylcyclobutadiene unlikely. We suggest the following mechanism for this reaction (Scheme I): initial attack of the sulfinylamine nitrogen atom at the 1(3)-position of the allylic moiety of **2** affords **7**, which by a successive ring closure at sulfur leads to sulfinamide **8**; ring-opening of **8** by fission of the C–N bond yields **9**,

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(2) Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265.

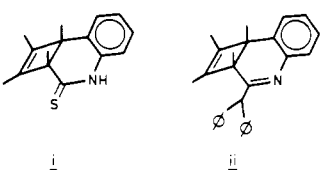
(3) Van Rantwijk, F. J.; Van der Stoel, R. E.; Van Bekkum, H. *Tetrahedron* **1978**, *34*, 569.

(4) Hogeveen, H.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 997.

(5) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 989.

(6) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 1909.

(7) (a) The structure of sulfinamide **4** has been elucidated by X-ray analysis.[6] ^{13}C NMR data of cyclobutene sp^3 carbon atoms in **4–6** (in ppm): **4**, 48.1 (s), 70.6 (s); **5**, 46.8 (s), 72.2 (s); **6**, 43.2 (s), 70.8 (d, J = 150 Hz). Compare with those of a structurally similar thioamide i[6] [48.6 (s) and 57.6 ppm (s)] and compound ii [47.0 (s) and 52.0 ppm (s)]. Comparison of these data clearly shows the absorption near 70 ppm in **4–6** to belong to the bridgehead carbon next to sulfur. Proof for the structure of **6** is found from the ^{13}C–^1H coupled spectrum, the absorption at 70.8 ppm being a doublet.



i ii

(b) The stereochemistry of the sulfinyl oxygen in **5** and **6** is believed to be the same as in **4** (X-ray structure[6]) because of the similarities in the ^1H NMR spectra. The following ^1H NMR data have been reported[6] ($CDCl_3$) for **4** (mp 185–187 °C): δ 1.25 (s, 3 H), 1.43 (s, 3 H), 1.59 (q, J = 1.1 Hz, 3 H), 1.81 (q, J = 1.1 Hz, 3 H), 6.26 (s, 1 H), 6.40–7.25 (m, 4 H). Compare the NMR data of the isomer of **4** with the sulfinyl oxygen in the exo position (mp 225 °C): δ 1.25 (q, J = 1.1 Hz, 3 H), 1.58 (br, 6 H), 1.60 (q, J = 1.1 Hz, 3 H), 6.58 (br s, 1 H), 6.38–7.38 (m, 4 H). Going from **4** to its exo isomer, one observes a remarkable upfield shift of one of the double bond CH_3 groups, accompanied by downfield shift of both bridgehead CH_3 absorptions to about 1.6 ppm. Looking at the corresponding data of **5** and **6** (Experimental Section), one finds a great resemblance with the endo isomer **4**.

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