Intramolecular Diels–Alder Reactions. VI.[1a] Syntheses of 3-Hydroxymethyl-2-naphthoic Acid Lactones

L. H. KLEMM,* R. A. KLEMM,[1b] P. S. SANTHANAM,[1c] AND D. V. WHITE[1d]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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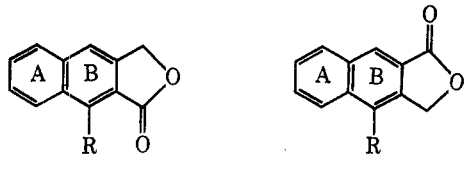
Twelve monoaryl enynic and diynic esters were synthesized and subjected to refluxing acetic anhydride. Seven underwent intramolecular Diels–Alder reactions. Propargyl phenylpropiolate (**9**) and phenylpropargyl propiolate cyclized to 3-hydroxymethyl-2-naphthoic acid lactone (**1b**), while *trans*-cinnamyl propiolate gave 3-hydroxymethyl-3,4-dihydro-2-naphthoic acid lactone. Derivatives of **1b** resulted from methoxy- and methylenedioxy-substituted compounds. Propargyl *trans*-cinnamate, allyl phenylpropiolate, and three derivatives of **9** did not cyclize. Purified samples of **9** and its derivatives exist as stable hydrates.

Previous studies in our laboratory[2–5] concerned the intramolecular Diels–Alder reaction of unsaturated diaryl esters of the type $Ar(C_2)CO_2CH_2(C_2)Ar'$, where each (C_2) unit is a $-CH{=}CH-$ or $-C{\equiv}C-$ group. For Ar and Ar′ = phenyl or substituted phenyl groups, the products formed have the skeletal structures of 1- or 4-phenyl-3-hydroxymethyl-2-naphthoic acid lactones (*i.e.*, of cyclolignan lactones) **1a** and **2a**, respectively (where ring B may be in the dihydro or tetrahydro form). In the present work we investigated the syntheses and cyclizations of unsaturated monoaryl esters



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a, R = Ph; **b**, R = H

of the types $H(C_2)CO_2CH_2(C_2)Ar'$ and $Ar(C_2)CO_2CH_2(C_2)H$. For Ar = Ar′ = Ph intramolecular Diels–Alder reactions should lead to 3-hydroxymethyl-2-naphthoic acid lactone (**1b** = **2b**) and its hydro products.

The esters prepared for cyclization and the cyclized products formed in our study are shown in Table I. Syntheses of the esters were effected by four different standard methods, as described in the Experimental Section. Ethyl 3,5-dimethoxyphenylpropiolate (**18**), needed to obtain **5** and **11**, was prepared from 3,5-dimethoxybenzaldehyde and triethyl iodophosphonoacetate. Compound **18** could not be obtained through initial treatment of ethyl *trans*-3,5-dimethoxycinnamate with bromine, a process which gave the 2-bromo derivative instead of the expected dibromopropionate (as occurs with ethyl *trans*-cinnamate,[6] as well as its 3,4-methylenedioxy and 3,4,5-trimethoxy derivatives).[7] In contrast to the other esters in Table I the four propargyl phenylpropiolates **9–12** retained water of hydration tenaciously. It appears that at least 0.25 mol of water is strongly bound to some common structural feature in these molecules.

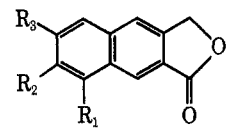
TABLE I

PRODUCTS FROM CYCLIZATION OF MONOARYL UNSATURATED ESTERS[a]

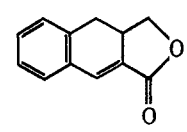
No.	Compd used: Formula[b]	Cyclization product	Yield,[c] %
	$H(C_2)CO_2CH_2(C_2)Ar'$ Series		
3	$HC{\equiv}CCO_2CH_2C{\equiv}CC_6H_5$	1b	2
4	3,4-Methylenedioxy-**3**	15	3*
5	3,5-Dimethoxy-**3**	16	10
6	*trans*-$HC{\equiv}CCO_2CH_2CH{=}CHC_6H_5$	17[d]	8
7	3,4-Methylenedioxy-**6**	15	13
8	3,5-Dimethoxy-**6**	16	5*
	$Ar(C_2)CO_2CH_2(C_2)H$ Series		
9	$C_6H_5C{\equiv}CCO_2CH_2C{\equiv}CH$	1b	14
10	3,4-Methylenedioxy-**9**	None	
11	3,5-Dimethoxy-**9**	None	
12	3,4,5-Trimethoxy-**9**	None	
13	*trans*-$C_6H_5CH{=}CHCO_2CH_2C{\equiv}CH$	None	
14	$C_6H_5C{\equiv}CCO_2CH_2CH{=}CH_2$	None	

[a] Cyclization conditions: refluxing acetic anhydride for 12–72 hr. [b] Compounds **4**, **5**, **7**, **8**, and **10–12** have substituents on the phenyl ring. [c] An asterisk denotes overall yields from the alcohol corresponding to the ester used. [d] From cyclization in a nitrogen atmosphere.

As in earlier studies[2–5] cyclization was effected by refluxing in acetic anhydride. Air oxidation probably accounts for formation of the aromatic compounds **15**



15, R_1 = H; R_2R_3 = OCH_2O
16, R_1 = R_3 = CH_3O; R_2 = H



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and **16** from the enynic esters **7** and **8**, respectively. Some **1b** was, likewise, isolated from cyclization of **6** in the presence of air. However, **6** gave the dihydronaphthalene lactone **17** when the reaction was conducted in an atmosphere of nitrogen. Even long refluxing did not give cyclization of **10–14**, while yields were low for **3–9**. In all of these intramolecular Diels–Alder reactions the aryl group must function as part of the "dienic moiety." Hence, one would expect esters **3–8** of the $H(C_2)CO_2CH_2(C_2)Ar'$ type to cyclize more readily than **9–14**, where the aryl group is part of the acidic moiety. Tendencies for the monoaryl compounds to

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cyclize are analogous to those in the diaryl series,[2-5] although overall yields from starting acidic and alcoholic components were generally higher in the diaryl cases.

Experimental Section[8]

Starting Materials.—Sodium propiolate was prepared by mixing equimolar amounts of anhydrous $NaHCO_3$ and propiolic acid in warm MeOH until CO_2 evolution ceased. The precipitated salt was collected by filtration and dried *in vacuo* for 2 days. Propiolyl chloride was prepared *in situ* by stirring (for 5 hr) an equimolar mixture of sodium propiolate and $SOCl_2$ in dry benzene. Formed *in situ* analogously from 3,4,5-trimethoxyphenylpropiolic acid[7] were the sodium salt and then (by stirring with excess $SOCl_2$ for 40 min, followed by repetitive addition and evaporation of benzene) the acid chloride. As needed, NaOEt was obtained by reacting a weighed amount of Na with excess absolute EtOH and removal of unreacted solvent *in vacuo*. Sodium salts of unsaturated alcohols were formed, in turn, by repetitive steps of addition of benzene to an equimolar mixture of the alcohol and NaOEt and then evaporation of the mixture to dryness.

Phenylpropargyl Chloride.[9]—To a cold (0°), stirred solution of 14.1 g (0.18 mol) of pyridine in 25 ml of $CHCl_3$ was added dropwise 20.2 g (0.17 mol) of $SOCl_2$. This solution was added dropwise, in turn, to a cold solution of 19.8 g (0.15 mol) of phenylpropargyl alcohol (Farchan) in 25 ml of $CHCl_3$. The mixture was stirred 10 min longer, refluxed for 2 hr, washed with water, dried (Na_2SO_4), and distilled to give 18.2 g (81%) of liquid: bp 62–65° (0.1 mm) [lit.[10] 51%, bp 99° (7 mm)]; ir ($CHCl_3$) 2230 (C≡C), 1250 cm^{-1} (C≡CCH$_2$Cl);[11] nmr (CCl_4) δ 4.26 (s, 2, CH_2Cl), 7.1–7.7 (m, 5, phenyl).

Ethyl *trans*-3,5-Dimethoxycinnamate.—Refluxing a solution of *trans*-3,5-dimethoxycinnamic acid (Aldrich) in 3% anhydrous ethanolic HCl[7] gave crystals (95%, mp 40–45°) converted to needles (mp 45–46°) on recrystallization from absolute EtOH: ir ($CHCl_3$) 1700 (ester C=O), 980 cm^{-1} (*trans*-CH=CH); nmr (CCl_4) δ 1.28 (t, 3, J = 7 Hz, CH_2CH_3), 3.72 (s, 6, 2 OCH_3), 4.20 (q, 2, CH_2CH_3), 6.34 (d, 1, J = 16 Hz, CH=CHC=O) which partially overlaps 6.3–6.7 (m, 4 total, including 3 aromatic H), *ca.* 7.55 (split d, CH=CHC=O).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.99; H, 6.62.

Methyl *trans*-3,5-Dimethoxycinnamate.—To a refluxing solution of 30.5 g of *trans*-3,5-dimethoxycinnamic acid in 340 ml of MeOH were added (in three portions over a period of 3.5 hr) total amounts of 20.2 g of KOH and 40 ml of Me_2SO_4. The mixture was evaporated nearly to dryness, treated with water, and extracted with ether. The ether layer was washed with aqueous $NaHCO_3$ solution and then with water and evaporated to yield 32.1 g (99%) of ester, mp 72–74.5°, obtained as prisms (mp 74.5–75.5°) on recrystallization from ether: nmr ($CDCl_3$) δ 3.78 (s, 9, 3 MeO), 6.38 (d, 1, J = 16 Hz, CH=CHC=O) which partially overlaps 6.48 (t, 1, J_m = 2.2 Hz, H-4), 6.64 (d, 2, H-2 and H-5), 7.59 (d, 1, CH=CHC=O).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.00; H, 6.51.

***trans*-3,5-Dimethoxycinnamyl Alcohol.**—To a stirred, cold (−78°) mixture of 1.37 g (0.036 mol) of $LiAlH_4$ and 100 ml of ether was added slowly a solution of 3.88 g (0.016 mol) of ethyl *trans*-3,5-dimethoxycinnamate in 50 ml of ether. The mixture was stirred at −78° for 2.5 hr longer, allowed to warm to room temperature, and, while still very cold, treated cautiously with water until a white solid formed. Evaporation of the dried ether layer plus ether extracts of the solid gave 2.9 g (85% pure by nmr spectrum, 78% yield) of nearly colorless liquid, which crystallized on standing. Recrystallization from CCl_4 gave needles: mp 54–55°; nmr ($CDCl_3$) δ 2.12 (broad s, 1, OH), 3.77 (s, 6, 2 OCH_3), 4.28 (d, 2, J = 4 Hz, CH_2), 6.2–6.6 (m, 5, aromatic and vinylic H).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.37; H, 7.48.

When the preceding reduction was run at 5°, both the vinylic and ester functions were affected to give **3-(3,5-dimethoxyphenyl)-1-propanol**: 73%, bp 146–154° (0.5 mm); analytically pure sample, bp 141° (0.4 mm) [lit.[12] bp 145–150° (3 mm)]; nmr (CCl_4) 1.5–1.9 (m, 2, $CH_2CH_2CH_2$), 2.3–2.7 (m, 2, CH_2OH), 3.2–3.6 (m, 3, $ArCH_2$ plus OH), 3.67 (s, 6, 2 MeO), 6.1–6.5 (m, 3, aromatic H).

Ethyl *trans*-2-Bromo-3,5-dimethoxycinnamate.—To a stirred solution of 2 g (8.5 mmol) of ethyl *trans*-3,5-dimethoxycinnamate in 10 ml of $CHCl_3$ was added (with cooling, over a period of 40 min) a solution of 1.4 g (8.8 mmol) of bromine in 5 ml of the same solvent. The orange color of the mixture persisted during an additional hour of stirring. Evaporation of the solvent and trituration of the residue with ligroin (60–90°) gave 2.1 g (79%) of crystals. Recrystallization from ligroin–benzene produced elongated prisms: mp 100–101.5°; positive Beilstein and permanganate tests, negative $AgNO_3$ test; ir ($CHCl_3$) 1710 (ester C=O), 980 cm^{-1} (*trans*-CH=CH); nmr (CCl_4) δ 1.32 (t, 3, J = 7 Hz, CH_2CH_3), 3.81 and 3.87 (2 s, 6, 2 MeO), 4.24 (q, 2, CH_2CH_3), 6.26 (d, 1, J = 16 Hz, CH=CHC=O) which partially overlaps 6.44 (d, J_m = 2.5 Hz, H-4), 6.68 (d, 1, H-6), 8.04 (d, 1, CH=CHC=O).

Anal. Calcd for $C_{13}H_{15}BrO_4$: C, 49.54; H, 4.80; Br, 25.36. Found: C, 49.32; H, 4.77; Br, 25.59.

***trans*-2-Bromo-3,5-dimethoxycinnamic Acid.**—Hydrolysis of preceding bromo ester was effected with aqueous methanolic KOH to give a white solid (39%), obtained as needles (mp 185–186°) on recrystallization from absolute EtOH: nmr ($CDCl_3$) δ 3.86 and 3.90 (2 s, 2 MeO), 6.42 (d, J = 16 Hz, CH=CH-C=O), 6.5–6.9 (poorly resolved, aromatic H), 8.30 (d, CH=CH-C=O); ir ($CHCl_3$) 1690 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_{11}BrO_4$: C, 46.01; H, 3.86; Br, 27.83. Found: C, 45.74; H, 3.80; Br, 27.61.

Ethyl 3,5-Dimethoxyphenylpropiolate (18).—To a cold (0°), stirred mixture of 0.3 mol of sodium triethyl iodophosphonoacetate (produced *in situ* by the stepwise procedure of Brown and Stevenson[13]) was added dropwise a solution of 50 g (0.3 mol) of 3,5-dimethoxybenzaldehyde (Aldrich) in 200 ml of glyme. The mixture was stirred for 10 hr while it warmed to room temperature. The solution was evaporated to a small volume, diluted with water, and extracted with ether. Evaporation of the ether extract produced a dark liquid layer (plus immiscible mineral oil) which distilled at 145–160° (0.5 mm) to give 40.8 g (58%) of colorless liquid which crystallized on standing at 6°. Recrystallizations from absolute EtOH and from CCl_4 gave prisms: mp 50–50.5°; ir (CCl_4) 2245 (C≡C), 1730 cm^{-1} (ester C=O); nmr (CCl_4) δ 1.32 (t, 3, J = 7 Hz, CH_2CH_3), 3.72 (s, 6, 2 OCH_3), 4.23 (q, 2, CH_2CH_3), 6.3–6.7 (m, 3, aromatic H).

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.80; H, 6.15.

3,5-Dimethoxyphenylpropargyl Alcohol.—To a cold (−78°), stirred mixture of 0.43 g (0.012 mol) of $LiAlH_4$ in 50 ml of dry ether was added, over a period of 20 min, 5 g (0.021 mol) of ester **18**. The mixture was stirred for 5 hr while it warmed to room temperature and was processed further as for the corresponding cinnamyl alcohol. Distillation at 170–180° (0.5 mm) gave 2 g (49%) of yellow liquid, which crystallized on standing at −5°. Recrystallization from CCl_4 gave white, sticky prisms: mp 38.5–40°; nmr (CCl_4) δ 2.77 (broadened s, 1, OH), 3.70 (s, 6, 2 OCH_3), 4.37 (s, 2, CH_2), 6.1–6.6 (m, 3, aromatic H).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 69.04; H, 6.55.

Propargyl *trans*-Cinnamate (13).—A mixture of cinnamoyl chloride (prepared from 3.7 g of *trans*-cinnamic acid), 1.4 g of propargyl alcohol, 40 ml of dry benzene, and 3 ml of pyridine was stirred for 10 hr, washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue gave 3.9 g (84%) of liquid: bp 117–119° (0.6 mm); ir (CCl_4) 3340 (≡CH), 1725 cm^{-1} (ester C=O); nmr (CCl_4) δ 2.52 (t, 1, J = 2.4 Hz, C≡CH),

(8) Microanalyses were performed by M-H-W Laboratories, Garden City, Mich., and Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were determined by means of a Beckman IR-5A or IR-7 spectrometer; and mass spectra were determined by means of a CEC Model 21-110 instrument at 70 eV. Unless otherwise indicated, nmr spectra were obtained by means of a Varian A-60 spectrometer, with tetramethylsilane used as internal standard. In three designated cases a Varian HA-100 instrument was used.

(9) Method developed by T. M. McGuire of this laboratory.

(10) M. J. Murray, *J. Amer. Chem. Soc.*, **60**, 2662 (1938).

(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1959, p 59.

(12) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3114 (1957); see also R. Huisgen, G. Seidl, and I. Wimmer, *Justus Liebigs Ann. Chem.*, **677**, 21 (1964); D. Nasipuri, R. Roy, and U. Rakshit, *J. Indian Chem. Soc.*, **37**, 369 (1960).

(13) D. Brown and R. Stevenson, *J. Org. Chem.*, **30**, 1759 (1965).

4.75 (d, 2, CH_2), 6.32 (d, 1, J = 16 Hz, CH=CHC=O), 7.1–7.5 (m, *ca.* 5, phenyl), 7.64 (d, 1, CH=CHC=O).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.32; H, 5.30.

Allyl Phenylpropiolate (14).—A mixture of 7.1 g of ethyl phenylpropiolate (Aldrich), 0.1 g of NaOEt, and 50–70 ml of allyl alcohol was refluxed for 2 hr and then fractionally distilled at a slow rate until 20 ml of residue remained. The residue was treated with water, neutralized with dilute hydochloric acid, and extracted with ether. Distillation of the dried extract gave 7.2 g (95%) of liquid product: bp 96–99° (0.5 mm); nmr (CCl_4) δ 4.66 (d, 2, J = 5.5 Hz, $CHCH_2O$), 5.0–6.4 (m, 3, CH_2=CH), 7.1–7.7 (m, 5, phenyl).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.03; H, 5.02.

Propargyl Phenylpropiolate (9). (a) By Ester Exchange.—In the preceding manner, except that propargyl alcohol was used in place of allyl alcohol, there was obtained 1.9 g (24%) of liquid: bp 60–63° (0.4 mm), redistilled at 68.5° (0.5 mm); ir (CCl_4) 3460 (weak, OH), 3320 (strong, ≡CH), 2130 (C≡C), 1730 cm^{-1} (ester C=O); nmr (CCl_4) δ 2.54 (t, 1, J = 2.5 Hz, C≡CH), 4.87 (d, 2, CH_2), 7.1–7.7 (m, 3, aromatic H), 7.8–8.2 (m, 2, aromatic H), water signal not apparent.

Anal. Calcd for $C_{12}H_8O_2 \cdot 0.5H_2O$: C, 74.60; H, 4.70. Found: C, 74.46; H, 4.78.

(b) *Via* **Acid Chloride.**—In the manner used for **13**, a mixture of phenylpropiolyl chloride,[4] propargyl alcohol, and pyridine was converted to **9**: bp 118–120° (0.8 mm); nmr ($CDCl_3$) δ 2.25 (t, 1, J = 2.5 Hz, C≡CH), 4.46 (d, 2, CH_2), 6.19 (s, *ca.* 0.4, $0.25H_2O$), 6.8–7.5 (m, 5, aromatic H).

Anal. Calcd for $C_{12}H_8O_2 \cdot 0.25H_2O$: C, 76.38; H, 4.54. Found: C, 76.44; H, 4.51.

Propargyl 3,4-Methylenedioxyphenylpropiolate (10).—This was prepared from methyl 3,4-methylenedioxyphenylpropiolate[7] and propargyl alcohol (as for **9**) to give a liquid product, bp 140–160° (0.5 mm), which solidified on standing: mp 45–55° (26%); ir (CS_2) 3320 (≡CH), 1730 (ester C=O), 1240 and 1040 (ArO), and 940 cm^{-1} (OCH_2O);[14] nmr (CCl_4) δ 2.40 (s, 0.6, *ca.* $0.25H_2O$), 2.62 (t, 1, J = 2.2 Hz, C≡CH), 4.84 (d, 2, CCH_2O), 5.98 (s, 2, OCH_2O), 6.72 (d, 1, J_o = 8 Hz, H-5), 7.33 (d, 1, J_m = 1.5 Hz, H-2), 7.56 (d of d, 1, H-6). Recrystallization from CCl_4 and then from absolute EtOH gave prisms: mp 61.5–62.5°; ir (CCl_4) 3670–3400 (OH), 3330 (≡CH), 1730 (ester C=O), 940 cm^{-1} (OCH_2O).

Anal. Calcd for $C_{13}H_8O_4 \cdot 0.5H_2O \cdot 0.25C_2H_5OH$: C, 65.19; H, 4.25. Found: C, 65.33; H, 4.05.

Propargyl 3,5-Dimethoxyphenylpropiolate (11).—This was obtained from ethyl ester **18** by exchange with propargyl alcohol and extraction of the product into benzene. Concentration of the solution gave crysals, mp 70–73° (25%), obtained as cream-colored needles (mp 73–74°) on recrystallizations from CCl_4 and absolute EtOH: ir (CCl_4) 3570–3400 (weak, broad, OH), 3320 (≡CH), 1720 cm^{-1} (ester C=O); nmr (CCl_4) δ 2.41 (t, 1, J = 2.5 Hz, C≡CH), 3.75 (broadened s, *ca.* 1.4, $0.75H_2O$), 3.81 (s, 6, 2 MeO), 4.84 (d, 2, CH_2), 6.55 (t, 1, J_m = 2 Hz, H-4), 7.12 (d, 2, H-2 and H-6).

Anal. Calcd for $C_{14}H_{12}O_4 \cdot 0.75H_2O$: C, 65.23; H, 5.28. Found: C, 65.05; H, 5.45.

Propargyl 3,4,5-Trimethoxyphenylpropiolate (12).—A mixture of 3,4,5-trimethoxyphenylpropiolyl chloride (prepared from 3.5 g of acid; *vide supra*), 0.87 g of propargyl alcohol, 1.3 mg of pyridine, and 20 ml of benzene was refluxed for 4.5 hr. The solution was washed with water and evaporated to give a product which crystallized from EtOH, yield 2.2 g (53%), mp 128–132.5°. Recrystallizations from CCl_4 and absolute EtOH gave faintly tan needles: mp 133.5–134°; ir (CCl_4) 3570–3400 (OH), 3320 (≡CH), 1720 cm^{-1} (ester C=O); nmr (CCl_4) δ 2.38 (t, 1, J = 2.5 Hz, C≡CH), 3.76 (s, 3, MeO at C-4), 3.82 (s, 6, 2 MeO), overlapping broadened band at *ca.* 3.8 (H_2O?), 4.71 (d, 2, CH_2), 6.73 (s, 2, H-2 and H-6).

Anal. Calcd for $C_{15}H_{14}O_5 \cdot 0.25H_2O$: C, 64.63; H, 5.24; O, 30.13. Found: C, 64.98; H, 5.12; O, 30.40.

3-Hydroxymethyl-2-naphthoic Acid Lactone (1b). (a) From Ester 9.—A solution of 1.42 g of $9 \cdot 0.25H_2O$ in 80 ml of Ac_2O was refluxed in a nitrogen atmosphere for 48 hr and then evaporated to dryness. Addition of MeOH to the residue gave 0.19 g (14%) of white plates, mp 202–206°, raised to 203.5–205° (lit.[15] 206°) on recrystallization from acetone–MeOH: ir ($CHCl_3$) 1760 cm^{-1} (γ-lactone); nmr ($CDCl_3$, HA-100) δ 5.48 (s, 2, CH_2), 7.26 (s, 1, H-4), 7.4–7.8 (m, 2, H-6 and H-7), 7.8–8.2 (m, 2, H-5 and H-8), 8.50 (s, 1, H-1).

Anal. Calcd for $C_{12}H_8O_2$: C, 78.15; H, 4.52. Found: C, 78.25; H, 4.38.

(b) *Via* **Phenylpropargyl Propiolate (3).**—A mixture of 0.81 g (8.8 mmol) of sodium propiolate, 1.32 g (8.8 mmol) of phenylpropargyl chloride, and 15 ml of dimethylformamide was refluxed for *only* 30 min in a nitrogen atmosphere and then evaporated to dryness. The residue was treated with CCl_4, filtered to remove NaCl, and chromatographed by means of silica gel–benzene to give **3** as a liquid: yield 0.7 g (43%); ir (CCl_4) 3320 (≡CH), 2130 (C≡C), 1730 cm^{-1} (ester C=O); nmr (CCl_4) δ 2.86 (s, 1, C≡CH), 4.95 (s, 2, CH_2), 7.1–7.6 (m, 5, phenyl).

Refluxing the crude **3** in Ac_2O gave a mixture of products from which was isolated 11 mg (2%) of **1b**, mp 204–205.5°, identified by direct comparison with product from method a.

3-Hydroxymethyl-3,4-dihydro-2-naphthoic Acid Lactone (17).—As in the preparation of ester **3**, equimolar quantities of sodium propiolate and *trans*-cinnamyl chloride (Eastman Kodak) gave, on chromatography, a crude product, purified further by evaporative distillation at 70–80° (0.1 mm) to give colorless, liquid ***trans*-cinnamyl propiolate (6)** (19%): ir (CCl_4) 3320 (≡CH), 2160 (C≡C), 1710 (ester C=O), 960 cm^{-1} (*trans*-CH=CH); nmr (CCl_4) δ 2.83 (s, 1, C≡CH), 4.67 (d, 2, J = 6 Hz, CH_2), 6.09 (d of t, 1, J_{trans} = 16 Hz, CH=CHCH$_2$), 6.59 (d, 1, CH=CHCH$_2$), 7.1–7.5 (broad s, 5, phenyl).

A solution of 2.6 g of **6** in 100 ml of Ac_2O was refluxed in a nitrogen atmosphere for 3 days and then evaporated. Extraction of the residue with boiling hexane, followed by concentration of solvent, addition of benzene (10% by vol), and cooling gave 0.21 g (8%) of **17**, obtained as a cream-colored powder: mp 136–138°, raised to 139–140° on recrystallization; ir ($CHCl_3$) 1760 cm^{-1} (γ-lactone); nmr ($CDCl_3$) δ 2.2–3.7 (m, 3, CH_2CHCH_2O), 4.04 and 4.78 (2 pseudotriplets, 1 each, CH_2O), 7.1–7.6 (m, 5, H-1 and aromatic H); mass spectrum[16] *m/e* at 186 (62), 156 (42), 155 (21), 142 (22), 141 (13), 129 (17), 128 (100), 127 (21), 63 (12), 51 (11), metastable peaks at 154, 131, 105, 104.

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.46; H, 5.41.

The nmr spectrum of **17** shows the same pattern of signals for aliphatic protons as found in 1-phenyl-3-hydroxymethyl-3,4-dihydro-2-naphthoic acid lactone.[4] The major fragments lost from electron impact on **17** are CH_2O, CO_2, CO, and H. The most abundant peak (*m/e* 128) corresponds to a naphthalene cation radical.

6,7-Methylenedioxy-3-hydroxymethyl-2-naphthoic Acid Lactone (15). (a) *Via* **Enynic Ester.**—An equimolar mixture of sodium 3,4-methylenedioxycinnamyl alkoxide[7] and propiolyl chloride in benzene was stirred for 3 hr, refluxed for 40 min, washed with water, and evaporated to dryness to give crude liquid ***trans*-3,4-methylenedioxycinnamyl propiolate (7)** (40%): ir ($CHCl_3$) 3320 (≡CH), 2270 (C≡C), 1730 (ester C=O), 940 cm^{-1} (OCH_2O);[14] nmr (CCl_4) δ 2.76 (s, C≡CH), 4.75 (d, J = 6 Hz, CH_2OC=O), 5.95 (s, OCH_2O), 6.0–7.0 (aromatic and vinylic H).

Refluxing this ester with Ac_2O, evaporation of the solvent, and treatment of the residue with petroleum ether gave crystals of **15**, mp 280–282° (13%), converted to a light yellow solid (mp 282–283°) on recrystallization from benzene–petroleum ether, CCl_4, and $CHCl_3$ plus sublimation at 0.5 mm: ir ($CHCl_3$) 1760 (γ-lactone), 930 cm^{-1} (OCH_2O); nmr ($CDCl_3$, HA-100) δ 5.42 (s, lactone CH_2), 6.12 (s, OCH_2O), 7.19 and 7.69 (2 s, H-4, H-5, H-8), 8.28 (s, H-1).

Anal. Calcd for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found: C, 68.76; H, 3.78.

(b) *Via* **Diynic Ester.**—Part a was repeated but with sodium 3,4-methylenedioxyphenylpropargyl alkoxide as the salt. A sample of the crude intermediate liquid **3,4-methylenedioxyphenylpropargyl propiolate (4)** showed an ir spectrum ($CHCl_3$): 3320 (≡CH), 2130 (C≡C), 1730 (ester C=O), 940 cm^{-1} (OCH_2O).[14] The overall yield of lactone **15** was 3%, mp 280–282°, identical with compound in method a as based on mixture melting point, as well as ir and nmr spectra.

6,8-Dimethoxy-3-hydroxymethyl-2-naphthoic Acid Lactone

(14) L. H. Briggs, L. D. Colebrook, H. M. Fales, and W. C. Wildman, *Anal. Chem.*, **29**, 904 (1957).

(15) F. Mayer, W. Schaefer, and J. Rosenbasch, *Arch. Pharm.* (*Weinheim*), **267**, 571 (1929); *Chem. Abstr.*, **24**, 839 (1930).

(16) Stable peaks of relative abundance less than 10% are not reported.

(16). (a) *Via* **Enynic Ester.**—In the foregoing manner was prepared the crude liquid ester *trans*-**3,5-dimethoxycinnamyl propiolate** (**8**): nmr ($CDCl_3$) δ 2.92 (s, C≡CH), 3.76 (s, 2 MeO), 4.80 (d, J = 6 Hz, CH_2), 6.2–6.7 (m, aromatic and vinylic H). Refluxing this ester in Ac_2O gave lactone **16**, mp 201–210° (5% overall). Sublimation at 0.5 mm raised the melting point to 212.5–214°.

(b) *Via* **Diynic Ester.**—Likewise was obtained the crude liquid ester **3,5-dimethoxyphenylpropargyl propiolate** (**5**): ir (CCl_4) 3320 (≡CH), 2130 (C≡C), 1720 cm^{-1} (ester C=O); nmr (CCl_4) δ 2.91 (s, C≡CH), 3.77 (s, 2 MeO), 4.25 (s, CH_2), 6.2–6.6 (m, aromatic H). Cyclization was effected in 10% yield to give lactone **16**: mp 201.5–204.5°, raised to 212.5–214° on recrystallization from benzene–petroleum ether plus sublimation at 0.5 mm; ir ($CHCl_3$) 1760 cm^{-1} (γ-lactone); nmr ($CDCl_3$, HA-100) δ 3.96 and 4.01 (2 s, 3 each, 2 MeO), 5.41 (s, 2, CH_2), 6.54 and 6.77 (2 d, 1 each, J_m = 2.5 Hz, H-5 and H-7), 7.64 (slightly split s, 1, H-4), 8.81 (s, 1, H-1); identical with product from method a as based on mixture melting point, as well as ir and nmr spectra.

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.06; H, 5.18.

Registry No.—**1b**, 4711-50-6; **3**, 29577-27-3; **4**, 29577-28-4; **5**, 29577-29-5; **6**, 29584-68-7; **7**, 29584-61-0; **8**, 29584-62-1; **9**, 29577-30-8; **10**, 29577-31-9; **11**, 29577-32-0; **12**, 29577-33-1; **13**, 29584-63-2; **14**, 29577-34-2; **15**, 5656-51-9; **16**, 29577-36-4; **17**, 29577-37-5; **18**, 29577-38-6; phenylpropargyl chloride, 3355-31-5; ethyl *trans*-3,5-dimethoxycinnamate, 29584-64-3; methyl *trans*-3,5-dimethoxycinnamate, 29584-65-4; *trans*-3,5-dimethoxycinnamyl alcohol, 29584-66-5; 3-(3,5-dimethoxyphenyl)-1-propanol, 1080-05-3; ethyl *trans*-2-bromo-3,5-dimethoxycinnamate, 29641-89-2; *trans*-2-bromo-3,5-dimethoxycinnamic acid, 29584-67-6; 3,5-dimethoxyphenylpropargyl alcohol 29577-41-1.

Electrolyte and Micellar Effects on Meisenheimer Complex Equilibria[1,2]

J. H. FENDLER,*[3a] E. J. FENDLER,[3a] AND M. V. MERRITT[3b]

Radiation Research Laboratories, Mellon Institute of Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and Department of Chemistry, Texas A & M University, College Station, Texas 77843

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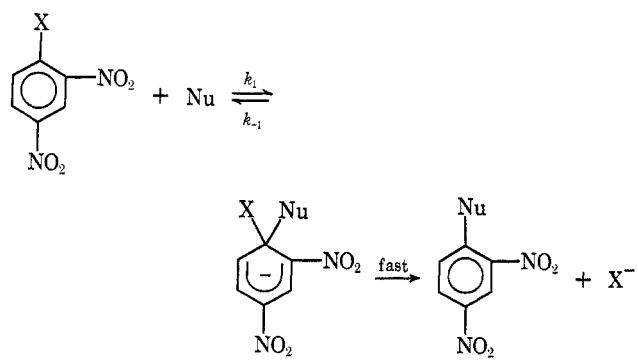
Electrolytes, with the exception of lithium salts, decrease the rate constant for the decomposition of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (**1**) in aqueous solutions. Cationic micellar CTAB and nonionic micellar Igepal CO-730 also decrease the decomposition rate of **1** by factors of 12 and 3.7, respectively, and anionic NaLS does not affect it. Both enthalpy and entropy factors are involved. The magnitude of micellar rate retardation is smaller for 1,1-dimethoxy-2,4-dinitro- (**2**) and 1,1-dimethoxy-2,4,5-trinitronaphthalene (**3**) complexes but is significantly greater for the spiro Meisenheimer complex of 1-(β-hydroxyethoxy)-2,4-dinitronaphthalene (**5**) than for **1**. The electrolyte and micellar effects originate from less destabilization of the initial state than of the transition state. CTAB enhances the equilibrium constants for the formation of the spiro complex of 1-(β-hydroxyethoxy)-2,4,6-trinitrobenzene and **5** by factors of 4750 and 250, respectively, while NaLS or Igepal have no appreciable effects. These results are compared critically to those obtained for other nucleophilic aromatic substitutions.

The effects of electrolytes and micelles on the reactions between nucleophiles and 2,4-dinitrohalobenzenes have been determined in aqueous solutions.[4] Such nucleophilic aromatic substitutions involve the rate-determining formation of an intermediate which decomposes rapidly to products. The relative effects



of electrolytes on the rate constants for the reaction of hydroxide ion with 2,4-dinitrochlorobenzene, for example, are $Me_4NCl > K_2SO_4 > Na_2SO_4 > KCl \sim H_2O > NaCl > NaBr \sim NaNO_3 > Li_2SO_4 > LiCl > LiBr > CH_3C_6H_4SO_3Na > LiClO_4$.[4] These electrolyte effects have been dissected into those on the activity coefficient of the aryl halide and those on the ratio of the activity coefficient of the hydroxide ion to that of the transition state. KCl, NaCl, NaBr, and LiBr increase f_{ArX} but decrease $f_{OH^-}/f^{\pm}$; $NaClO_4$, on the other hand, decreases both f_{ArX} and $f_{OH^-}/f^{\pm}$.

Cationic micellar surfactants were found to enhance k_1 by factors of *ca.* 60–80, the magnitude of the rate decrease by anionic surfactants was somewhat more modest, and neutral micellar surfactants had no effect on k_1.[4,5]

In order to obtain information on the effects of electrolytes and micelles on nucleophilic aromatic substitutions in which the rate-determining step is governed by the decomposition of the complex, we have investigated these effects on the rates of decomposition of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (**1**). Since micellar catalysis involves specific substrate–micelle interactions, we have also examined the influence of micellar surfactants on the rates of decomposition of the methoxyl complexes of 1-methoxy-2,4-dinitronaphthalene (**2**) and 1-methoxy-2,4,5-trinitronaphthalene (**3**) and of the spiro Meisenheimer

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(2) Reported, in part, preliminarily by E. J. Fendler and J. H. Fendler, *Chem. Commun.*, 816 (1970).

(3) (a) Texas A & M University; (b) Department of Chemistry, Franklin and Marshall College, Lancaster, Pa. 17604.

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(5) For reviews of micellar effects on reaction rates, see E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969), and E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).