Electroreduction of α,β-Unsaturated Esters. II. Syntheses of 2,3-Diaryl-5-oxocyclopentane-1-carboxylates by Hydrodimerization of Cinnamates[1a]

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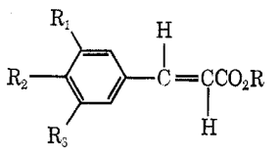
2,3-Diaryl-5-oxocyclopentane-1-carboxylates (**4**) were synthesized in yields of 7–60% by electrolytic hydrodimerization of trans cinnamate esters in anhydrous acetonitrile–tetraethylammonium bromide at constant, controlled cathode potential. For ethyl cinnamate as substrate the hydrodimer was found to have the *trans*-diphenyl geometry. A mechanism for the formation of **4**, involving steps of (a) β,β coupling of oriented anion radicals at the electrode surface, (b) protonation of the dinegative anion by an available proton source, and (c) Dieckmann-type cyclization, is suggested. When ethyl 3′,4′-dimethoxycinnamate was hydrodimerized in the presence of ethyl crotonate (nonreducible at the cathode potential used), the latter underwent concurrent catalyzed dimerization, presumably by means of acid–base interaction.

In a previous paper[2] we reported that trans cinnamate esters show two polarographic waves (presumed to involve one electron each) in anhydrous acetonitrile–tetraethylammonium bromide. Addition of a proton source (such as water) to the solvent–electrolyte caused shift of the half-wave reduction potentials to less negative values—sometimes even to the point of coalescence of the two waves into one (of twice the height). In two cases investigated, macroscale reductions conducted at a cathode potential somewhat more negative than the second (or coalesced wave) gave simple hydrogenation of the conjugated carbon–carbon double bond. We now report the results of macroscale syntheses at a cathode potential maintained between the first and second waves in the same anhydrous solvent–electrolyte.

In preparation for the electrosyntheses, polarographic investigations were conducted on a series of eight trans compounds, *viz.*, cinnamate esters **1a–f**, ethyl crotonate



1a, $R_1 = R_2 = R_3 = H$; R = Et
b, $R_1 = R_2 = R_3 = H$; R = $CH_2C{\equiv}CH$
c, $R_1 = R_2 = R_3 = H$; R = $CH_2C{\equiv}CPh$
d, $R_1 = H$; $R_2 = R_3 = OCH_3$; R = Et
e, $R_1 = H$; $R_2 = R_3 = OCH_3$; R = $CH_2C(H){=}C(H)$–3,4-di-OCH_3-phenyl
f, $R_1 = H$; $R_2R_3 = OCH_2O$; R = Et

(**2**), and 3′,4′-dimethoxycinnamyl alcohol (**3**) in the aforementioned solvent system. Data are reported in Table I. From this table one notes that cinnamate esters with or without alkoxy substitutents on the phenyl ring and with either saturated or unsaturated R groups in the alcoholic moiety show two reduction waves at −1.76 to −1.94 and −2.16 to −2.31 V under anhydrous conditions. On this basis a constant cathode potential in the range of −2.06 ± 0.06 V was selected for macroscale studies on the seven esters shown in Table II. Coulometry on **1d** at −2.06 V indicated the uptake of *ca.* 1.07 electrons in the first reduction wave.

TABLE I
POLAROGRAPHIC HALF-WAVE REDUCTION POTENTIALS[a] FOR SOME MODEL COMPOUNDS

Substrate	Solvent–electrolyte[b]	First wave[c] $-E_{1/2}$	Second wave[c] $-E_{1/2}'$
1a	A	1.86	2.23
1b	A	1.77	2.16
	B	1.71	1.91
1c	A	1.76	*d*
	B	1.67	1.89
1d	A	1.94[e]	2.26[e]
1e	A	1.87	2.31
	B	1.79	2.29
1f	A	1.91	2.25
	B	1.80	2.00
2	A	2.37	*f*
3	A	2.54	*f*
	B	2.45	*f*

[a] In volts *vs.* the saturated calomel electrode. [b] A, 0.05 *M* Et_4NBr in anhydrous MeCN; B, solvent A diluted with 3.85 vol. % water. [c] Unless otherwise noted, the first and second waves have approximately equal heights. [d] Poor wave. [e] Data from ref 2. [f] No second wave is observed.

TABLE II
CYCLIC HYDRODIMERIZATION PRODUCTS FROM ELECTROREDUCTION OF TRANS CINNAMATE ESTERS IN ANHYDROUS MeCN–Et_4NBr

Cinnamate used: Aryl substituents	Cinnamate used: R group	Cinnamate used: No.	Cyclic hydrodimer formed: No.	Cyclic hydrodimer formed: Yield,[a] %	Cyclic hydrodimer formed: Mp,[a] °C
3,4-OCH_2O	Me	**1g**	**4g**	60	160–162.5
None	Et	**1a**	**4a**	52	105–106.5
None	$PhC{\equiv}CCH_2$	**1c**	**4c**[b]	8	159–161
None	*trans*-$PhCH{=}CHCH_2$	**1h**	**4h**[b]	13	126–128
3,4-di-MeO	Et	**1d**	**4d**[c]	52	110.5–112
3,4-di-MeO	*t*-Bu	**1i**	**4i**	7	118–123
3,5-di-MeO	Et	**1j**	**4j**	28	115.5–117.5

[a] Of product after one crystallization from an appropriate solvent. [b] Hydrolysis products of the substrate molecule were also isolated. [c] Dihydro-**1d** was also isolated.

It is apparent from Table I that the electrons which enter the substrate molecule are accommodated by the cinnamoyl moiety as a whole. Thus, changing the substrate from ethyl cinnamate (**1a**) to ethyl crotonate

(1) (a) This investigation was supported by Grant No. GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service. (b) Research Assistant, 1968–1971; NDEA Fellow, 1971–1972.

(2) L. H. Klemm, D. R. Olson, and D. V. White, *J. Org. Chem.*, **36**, 3740 (1971).

(2) makes electroreduction considerably more difficult. Also the high reduction potential of 3′,4′-dimethoxycinnamyl alcohol (3) contrasts with the lower values of both $E_{1/2}$ and $E_{1/2}'$ for **1e**.

For each substrate used in these studies a crystalline cyclic hydrodimer (4) was isolated, according to balanced cathodic equation 1, where BH is a proton source (*e.g.*, Et_4N^+, CH_3CN, or even traces of H_2O). The structure of **4** was assigned to each product on the basis

$$2\mathbf{1} + 2e^- + BH \longrightarrow \mathbf{4} + OR^- + B^- \quad (1)$$

of elemental analyses, proton nmr spectra, the presence of two carbonyl absorption bands at 1720–1735 and 1750–1765 cm^{-1}, and a positive ferric chloride color test for the presence of an enol.[3] In addition, products **4a** and **4d** were characterized in other ways. Thus, the mass spectrum of **4d** was consistent with the proposed structure and the product was readily hydrolyzed and decarboxylated (by means of refluxing aqueous ethanolic HBr) to the corresponding 3,4-diarylcyclopentanone (**5**).

Compound **4a** has been described in the literature on two previous occasions. Totton, *et al.*,[4] obtained a 10% yield of this product by treating ethyl cinnamate with sodium under conditions of the acyloin condensation. While our studies were in progress, Baizer, *et al.*,[5] reported the formation of a mixture of products (including **4a**, ethyl β-phenylpropionate, recovered ethyl cinnamate, and diethyl 2-benzyl-3-phenylglutarate, in unstated yields) from electrolytic reduction of **1a** in aqueous DMF–tetraethylammonium *p*-toluenesulfonate. As a synthetic procedure for **4a**, electrolysis in acetonitrile appears to be the method of choice.

Hydrolytic decarboxylation of **4a** (in the foregoing manner) produced *trans*-3,4-diphenylcyclopentanone (**6**, 85% yield). Since it is unlikely that conditions of hydrolysis would cause stereochemical inversion at C-2 or C-3 in **4a**, the keto ester is also assigned the trans geometry at these two carbons (see structure **4a′**). The basic conditions attendant to the electrolytic formation of **4a** should foster equilibration at C-1. Contrariwise, these conditions should not alter the stereochemistries at C-2 and C-3. It therefore appears that the trans geometry of **4a′** is established during the process of hydrodimerization *per se*.

Baizer, *et al.*,[5] proposed that hydrodimerization may involve coupling of an anion radical with a neutral molecule. In fact his group found[6] that cross-coupling between two α,β-unsaturated esters can sometimes be effected at a cathode potential which is ostensibly too anodic to reduce directly one of the two components. In an allied experiment we electrolyzed a mixture of **1d** and ethyl crotonate (**2**) (molar ratio, **2**:**1d** = 7.2:1) in anhydrous MeCN–Et_4NBr at a cathode potential of −2.03 V. Two products were isolated, *viz.*, hydrodimer **4d** and a dimer of **2**, diethyl 2-ethylidene-3-methylglutarate (**7**, 49% yield based on total **2** present or 1.7 mol of **7** per 1 mol of **1d** used). No cross-coupled products were identified. Dimer **7** has been prepared by Shabtai and Pines[7] by treatment of **2** with potassium–benzyl potassium at 110°. Under their reaction conditions they proposed that dimerization is initiated by metalation of **2** at C-2, and the attendant carbanion then undergoes Michael addition to a second molecule of **2**. In our electrolysis we favor the mechanism shown in Scheme I, where A^{2-} is an electrochemically generated

SCHEME I

$$A^{2-} + \underset{\mathbf{2}}{CH_3CH{=}CHCO_2Et} \rightleftharpoons AH^- + \bar{C}H_2CH{=}CHCO_2Et \leftrightarrow CH_2{=}C\bar{H}CHCO_2Et \quad (\mathbf{8})$$

$$\mathbf{8} + \mathbf{2} \xrightleftharpoons{\text{Michael addition}} EtO_2CCH(CH_2{=}C)CH\bar{C}HCO_2Et \quad (\mathbf{9})$$

$$\mathbf{9} + \mathbf{2} \rightleftharpoons EtO_2CCH(CH_2{=}C)CHCH_2CO_2Et + \mathbf{8}$$

$$\mathbf{8} \text{ (proton transfer)} \rightarrow EtO_2CC(CH_3)(CH)CHCH_2CO_2Et \quad (\mathbf{7})$$

anion (*vide infra*), which serves as initiator for a chain process of base-catalyzed dimerizations of **2** by abstraction of a γ proton from the latter. This type of mechanism was considered to represent only a "remote possibility" under the conditions used by Shabtai and Pines.

It was found that initiation of the dimerization of **2** occurs in the vicinity of the cathode and not in the bulk solution, for, when cinnamate **1d** was first hydrodimerized in the usual way and the resultant catholyte solution was then stirred with **2** (open circuit), no dimer **7** was detected. On this basis, we suggest that dimerization initiator A^{2-} is generated by a cathodic process.

Bard, *et al.*[8] offer strong evidence that the hydrodimerization of diethyl fumarate in DMF–$(n\text{-}Bu)_4NI$ (with or without added water) occurs through direct coupling of electrochemically generated anion radicals. The resultant dinegative anion is presumed to protonate rapidly. Since their findings should apply to our sys-

(3) S. Soloway and S. H. Wilen, *Anal. Chem.*, **24**, 979 (1952).
(4) E. L. Totton, R. C. Freeman, H. Powell, and T. L. Yarboro, *J. Org. Chem.*, **26**, 343 (1961).
(5) J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 749 (1969).
(6) M. M. Baizer, J. P. Petrovich, and D. A. Tyssee, *J. Electrochem. Soc.*, **117**, 173 (1970).
(7) J. Shabtai and H. Pines, *J. Org. Chem.*, **30**, 3854 (1965). See also ref 16 for conversion of **2** to **7** by means of NaOEt in ether.
(8) W. J. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, **118**, 874 (1971); V. J. Puglisi and A. J. Bard, *ibid.*, **119**, 829 (1972).

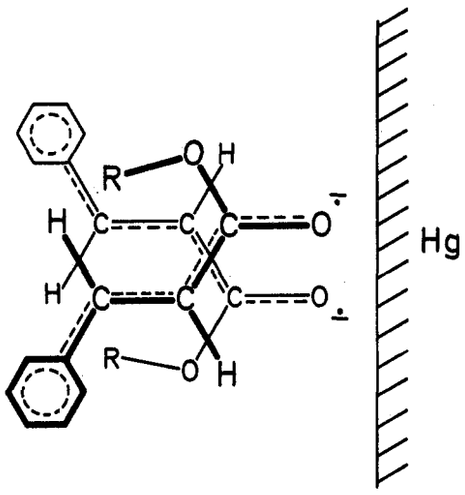
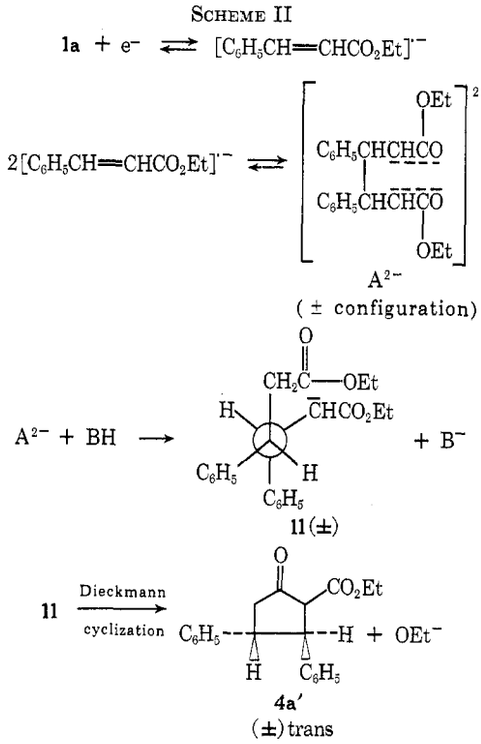


Figure 1.—Geometric relationship for β,β coupling of cinnamate ester anion radicals at the mercury cathode.

tem as well, we propose that A^{2-} is in fact the β,β-coupled product from two cinnamate ester anion radicals. The overall mechanistic scheme for the formation of cyclic hydrodimer **4a′** from ethyl cinnamate (**1a**) is then depicted in Scheme II. In this

SCHEME II



scheme, the trans stereochemistry of the final product (**4a′**) is established at the point where the two anion radicals undergo β,β coupling. Protonation on one of the α-carbon atoms gives (±) anion **11**, with the structure of an intermediate which is proposed in the familiar Dieckmann cyclization.[9] Completion of the cyclization then yields **4a′**.

It now becomes possible to rationalize the configuration of A^{2-} in terms of a preferred geometric relationship between the two reacting anion radicals. We propose that this geometry is, in fact, established between a pair of substrate molecules as they approach the electrode (*i.e.*, enter the electrical double layer adjacent to the electrode surface). While it is unnecessary that these molecules assume a preferential orientation with respect to the electrode surface itself (but only with respect to one another) in order to achieve this geometric goal, we visualize that the long axes of the cinnamate moieties approximate perpendicularity to this surface (as depicted in Figure 1). In this figure the carbonyl oxygen atoms are directed toward the electrode and approach closely enough for direct charge transfer to occur. The substrate molecules lie in close proximity in parallel planes, but with the bulky phenyl group of one molecule over the β-hydrogen atom of the other molecule. In this orientation β,β coupling could occur simultaneously with the addition of an electron to each molecule. Figure 1 shows the R groups oriented away from the electrode surface (or electrical double layer) toward the less polarizing bulk solution. In such a molecular conformation (preferred at the electrode surface, but not in the bulk solution) long or bulky R groups should interfere sterically with the close approach of the cinnamate moieties which is needed to permit β,β coupling. Thus, in a general way, Figure 1 accounts for the marked decrease in yield of cyclic hydrodimer when R is changed from Et (in **1a** or **1d**) to cinnamyl (**1h**) and phenylpropargyl (**1c**) or to *t*-Bu (**1i**), respectively. It is noteworthy that Totten[4] also obtained the trans isomer **4a′** under conditions where surface dimerization (on sodium particles) of oriented anion radicals may be invoked. It is likely that the product isolated by Baizer[5] also has the structure **4a′**.

Experimental Section[10]

Starting Materials and Apparatus.—Substrate molecules **1a–h**, **1j**, **2**, and **3** were available either commercially or from previous synthesis in our laboratory.[11,12] The acid chloride[2] from 3.11 g of *trans*-3′,4′-dimethoxycinnamic acid was stirred overnight with excess *tert*-butyl alcohol in dry benzene and the solvent was evaporated. A solution of the residue in $CHCl_3$ was washed with 10% aqueous $NaHCO_3$, dried, and evaporated to yield 3.8 g of crude, liquid ***tert*-butyl *trans*-3′,4′-dimethoxycinnamate** (**1i**), purified further by evaporative distillation at 140° (0.1 mm): ir ($CHCl_3$) 1690 (C=O) and 985 cm^{-1} (*trans*-CH=CH); pmr (CCl_4) δ 1.50 (s, 9, *t*-Bu), 3.82 (s, 6, 2 CH_3O), 6.14 (d, 1, J = 16 Hz, CH=CHC=O), 6.6–7.1 (m, 3, aromatic H), 7.46 (d, 1, CH=CHC=O).

The apparata and general procedures for polarography and macroscale synthesis at constant cathode potential were described earlier.[2] The apparatus for coulometry of **1d** was modified from that used for electrosynthesis in that the Redox-O-Trol was replaced by a circuit containing a manually operated dc rheostat and a gas coulometer,[13] while the cathode potential was periodically checked by means of a potentiometer. Correction for background current was made to the coulometric reading.

Electrohydrodimerization (General Procedure).—To the catholyte of 50 ml of preelectrolyzed 0.1 M Et_4NBr in anhydrous

(9) J. P. Schaefer and J. J. Bloomfield, *Org. React.*, **15**, 1 (1967).

(10) Microanalyses were performed by Clark Microanalytical Laboratories, Urbana, Ill., M-H-W Laboratories, Garden City, Mich., and Dr. Susan Rottschaefer, University of Oregon. Infrared spectra were determined by means of a Beckman IR-5A or IR-7 spectrometer; mass spectra, by means of a CEC Model 21-110 instrument at 70 eV; and pmr spectra, by means of a Varian A-60 or HA-100 spectrometer, with tetramethylsilane as internal standard.

(11) L. H. Klemm, K. W. Gopinath, G. C. Karaboyas, G. L. Capp, and D. H. Lee, *Tetrahedron*, **20**, 871 (1964).

(12) L. H. Klemm, R. A. Klemm, P. S. Santhanam, and D. V. White, *J. Org. Chem.*, **36**, 2169 (1971).

(13) J. J. Lingane, *J. Amer. Chem. Soc.*, **67**, 1916 (1945).

MeCN was added (in one portion) 0.8–3.2 g of cinnamate ester 1 and electroreduction was conducted at a constant cathode potential of -2.06 ± 0.06 V (*vs.* a saturated calomel electrode) without external cooling of the cell until the current had fallen to background level (10–25 min). (In a few runs a solution of the ester in MeCN was added dropwise to the cathode chamber while electroreduction was proceeding, but this method gave less satisfactory results and required longer reaction times.) The catholyte and anolyte solutions were combined and evaporated. The residue was extracted with a mixture of $CHCl_3$ (or CH_2Cl_2) and water, usually 75 and 25 ml, respectively. Normally, the water layer was discarded, but, in a few cases, it was acidified to pH 1 and examined for acidic products. The dried organic layer was evaporated to give a residue which was chromatographed on a column of silica gel (3–10 g) with $CHCl_3$, EtOAc, or (in the case of **4c** only) benzene. The hydrodimer **4** was eluted in early fractions, recrystallized once to give the yield reported in Table II, and then recrystallized further to analytical purity. The hydrodimer gave a positive $FeCl_3$ test (violet)[3] and showed two carbonyl absorptions at 1720–1735 and 1750–1765 cm^{-1}. In runs with **1c** and **1h** later chromatographic effluent fractions were examined for the presence of by-products. Details on individual products are presented in subsequent paragraphs.

Methyl 2,3-Bis(3,4-methylenedioxyphenyl)-5-oxocyclopentanecarboxylate (4g).—Crystallizations of the product from methanol and ethanol gave flat prisms: mp 158–160°; ir ($CHCl_3$) 935 cm^{-1} (OCH_2O); pmr ($CDCl_3$) δ 2.5–3.0 (m, 2, 2 H-4), 3.72 (s, 3, Me) which overlaps 3.0–4.1 (m, 3, H-1, H-2, H-3), 5.90 (s, 4, 2 OCH_2O), 6.66 (broad s, 6, aromatic H).

Anal. Calcd for $C_{21}H_{18}O_7$: C, 65.96; H, 4.75. Found: C, 66.05; H, 4.75.

When the electrolysis of **1g** was conducted at 0°, only a 10% yield of **4g** was obtained.

Ethyl *trans*-2,3-Diphenyl-5-oxocyclopentanecarboxylate (4a).—The product from the CH_2Cl_2 extraction was crystallized directly (without intervening chromatography) a single time from aqueous MeOH to give fine needles: mp 105–106.5° (lit.[4] mp 102–103°, lit.[5] mp 105–107°); pmr ($CDCl_3$) δ 1.20 (t, J = 7 Hz, OCH_2CH_3), 2.6–3.0 (m, 2 H-4), 3.0–4.0 (m, H-1, H-2, H-3), 4.17 (q, OCH_2CH_3), 7.20 (s, 2 phenyl groups).

***trans*-3,4-Diphenylcyclopentanone (6).**—A solution of 115 mg of **4a** in 2 ml of EtOH and 1.3 ml of 48% HBr was refluxed for 2 hr, diluted with 10 ml of H_2O, and extracted with 25 ml of $CHCl_3$. Evaporation of the dry ($MgSO_4$) organic layer gave 75 mg (85%) of **6** as needles: mp 177–179° (lit.[14] mp 178–179° for trans isomer, 106° for cis isomer); ir ($CHCl_3$) 1745 cm^{-1}; pmr ($CDCl_3$) δ 2.3–3.0 (m, 4, 2 methylene groups), 3.2–3.6 (m, 2, H-3, H-4), 6.9–7.3 (m, 10, aromatic H), consistent with the reported[15] pmr spectrum of the trans isomer, but not with that of the cis isomer.

Ethyl 2,3-Bis(3,4-dimethoxyphenyl)-5-oxocyclopentanecarboxylate (4d).—The product was crystallized from ether and then EtOH–ether to give needles: mp 115–116°; pmr ($CDCl_3$) δ 1.23 (t, 3, J = 7 Hz, OCH_2CH_3), 2.5–3.0 (m, 2, 2 H-4), 3.74, 3.77, and 3.83 (3 s, 12, 4 MeO) plus 4.18 (q, 2, OCH_2CH_3) superimposed on 3.2–4.4 (m, 3, H-1, H-2, H-3), 6.5–6.9 (m, 6, aromatic H); mass spectrum m/e (rel intensity) 428 (82, M^+), 382 (48), 356 (15), 236 (47, **1d**$^+$), 191 [53, $(CH_3O)_2C_6H_3CH{=}CHC{=}O^+$], 164 [100, $(CH_3O)_2C_6H_3CH{=}CH_2^+$].

Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.27; H, 6.59. Found: C, 67.49; H, 6.68.

3,4-Bis(3,4-dimethoxyphenyl)cyclopentanone (5).—Hydrolytic decarboxylation of **4d** in the manner used with **4a** and crystallization of the product from EtOH gave **5** (68%): mp 88–91°, raised to 96–97° (needles) on recrystallizations from EtOH and then from ether–petroleum ether (bp 30–60°); ir ($CHCl_3$) 1740 cm^{-1}; pmr ($CDCl_3$) δ 2.5–2.9 (m, 4, 2 CH_2 groups), 3.1–3.6 (m, 2, H-3, H-4), 3.76 and 3.83 (2 s, 6 each, 4 MeO), 6.5–6.9 (m, 6, aromatic H).

Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.76; H, 6.79. Found: C, 71.04; H, 6.81.

Ethyl 3-(3,4-Dimethoxyphenyl)propionate (10) from Electroreduction.—In an electroreduction of 0.53 g of **1d** (reaction time 70 min) the water extract was evaporated to dryness and the residue was refluxed with a mixture of 50 ml of absolute EtOH and 0.7 ml of concentrated H_2SO_4 for 5 hr. After evaporation of most of the solvent the residual solution was neutralized with aqueous $NaHCO_3$ and extracted with $CHCl_3$. Evaporation of the solvent left 120 mg (22%) of crude **10**, purified further by evaporative distillation at 100° (0.4 mm): ir ($CHCl_3$) 1730 cm^{-1}; pmr ($CDCl_3$) δ 1.23 (t, J = 7 Hz, OCH_2CH_3), 2.4–3.1 (m, CH_2CH_2), 3.85 (s, 2 MeO), 4.13 (q, OCH_2CH_3), 6.77 (s, aromatic H).

Refluxing a mixture of 100 mg of **10**, 10 mg of NH_4Cl, and 1 ml of benzylamine for 1 hr gave (after acidification and extraction into $CHCl_3$) ***N*-benzyl-3-(3,4-dimethoxyphenyl)propionamide,** obtained as needles after recrystallizations from aqueous acetone, hexane–toluene, and hexane–benzene: mp 80.5–81.5°; ir (KBr) 3280 (NH), 1640, and 1550 cm^{-1} (amide); pmr ($CDCl_3$) δ 2.3–3.1 (m, 4, CH_2CH_2), 3.76 and 3.80 (s, 6, 2 MeO), 4.35 (d, 2, J = 5.5 Hz, benzyl CH_2), 6.1–6.5 (broad, NH), 6.73 (s, 3, aromatic H of dimethoxyphenyl ring), 7.0–7.4 (m, 5, benzyl aromatic H).

Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07; N, 4.68. Found: C, 72.49; H, 6.72; N, 4.69.

Electroreduction by simultaneous addition to the catholyte of solutions of 4.4 mmol of **1d** in 25 ml of MeCN and 2.2 mmol of anhydrous HBr in 10 ml of MeCN gave **4d** (22%) and **10** (20%).

Ethyl 2,3-Bis(3,5-dimethoxyphenyl)-5-oxo-cyclopentane-1-carboxylate (4j).—This product formed clumps of needles from acetone-hexane: mp 112–113°; pmr (CCl_4) δ 1.22 (t, 3, J = 7 Hz, OCH_2CH_3), 3.66 and 3.71 (2 s, 12, 4 MeO) superimposed on 2.4–3.8 (m, 5, H-1 to H-4), 4.14 (q, 2, OCH_2CH_3), 6.1–6.4 (m, 6, aromatic H).

Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.27; H, 6.59. Found: C, 67.07; H, 6.63.

***tert*-Butyl 2,3-Bis(3,4-dimethoxyphenyl)-5-oxo-cyclopentane-1-carboxylate (4i).**—This substance formed needles from ether: mp 123–124°; pmr ($CDCl_3$) δ 1.17 and 1.43 (2 s, 9, *t*-Bu), 3.75–3.95 (m, 12, 4 MeO) superimposed on 2.6–4.0 (m, 5, H-1 to H-4), 6.6–6.9 (m, 6, aromatic H).

Anal. Calcd for $C_{26}H_{32}O_7$: C, 68.40; H, 7.07. Found: C, 68.61; H, 6.91.

Phenylpropargyl 2,3-Diphenyl-5-oxo-cyclopentane-1-carboxylate (4c).—The compound crystallized as needles from MeOH: mp 164.5–165.5°; pmr ($CDCl_3$) δ 2.5–3.1 (m, 2, 2 H-4), 3.2–4.2 (m, 3, H-1, H-2, H-3), 4.96 (s, 2, $C{\equiv}CCH_2$), 7.21 (broad s, 10, phenyl groups at C-2 and C-3), 7.37 (broad s, 5, $C_6H_5C{\equiv}C$).

Anal. Calcd for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62. Found: C, 82.16; H, 5.71.

The chromatographic fraction which followed **4c** off the column contained phenylpropargyl alcohol (14%), identified by spectral comparison with an authentic sample. Extraction of the acidified water layer from processing of the electroreduction mixture gave *trans*-cinnamic acid (29%), identified by mixture melting point with an authentic sample. It is uncertain at which point in the procedure these hydrolysis products are formed.

***trans*-Cinnamyl 2,3-Diphenyl-5-oxo-cyclopentane-1-carboxylate (4h).**—This compound formed needles on repetitive crystallizations from ether: mp 128–129°; ir ($CHCl_3$) 965 cm^{-1} (trans CH=CH); pmr ($CDCl_3$) δ 2.6–3.0 (m, 2, 2 H-4), 3.2–4.1 (m, 3, H-1, H-2, H-3), 4.79 (d, 2, J = 5 Hz, cinnamyl CH_2), 5.8–6.9 (m, 2, 2 vinyl H), 7.21 (broad s, 10, phenyl groups at C-2 and C-3), 7.32 (broad s, 5, $C_6H_5CH{=}$).

Anal. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10. Found: C, 81.93; H, 6.00.

As in the preparation of **4c**, hydrolysis by-products of *trans*-cinnamyl alcohol (50%) and *trans*-cinnamic acid (24%) were isolated and identified.

Electroreduction of 1d in the Presence of Ethyl Crotonate (2).—After preelectrolysis (at -2.03 V) of a mixture of the usual catholyte plus 4.1 g (36 mmol) of **2**, electroreduction was continued at the same potential while a solution of 1.19 g (5 mmol) of **1d** in 15 ml of MeCN was added (over a period of 15 min) and for 5 min longer. The total solution was evaporated, the residue was extracted with CH_2Cl_2–H_2O, and the product from evaporation of the organic phase was chromatographed on silica gel with successive elution by (a) hexane, (b) 5% $CHCl_3$ in hexane, (c) benzene, and (d) ether. Pmr analysis of effluents a and b indicated that only aliphatic protons were present. Rotary evaporation at 80° of combined effluents a and b to constant weight (compound **2** is volatile under these conditions) gave 2.02 g (49%, based on total **2** used) of **diethyl 2-ethylidene-3-methylglutarate (7):** ir ($CHCl_3$) 1640 (conjugated C=C), 1710, and 1730 cm^{-1} (ester C=O groups); pmr (neat) δ 1.17

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and 1.25 (2 overlapping t, superimposed on d, 9, 2 OCH_2CH_3 plus CH_3CHCH_2), 1.82 (d, 3, J = 7 Hz, $=CHCH_3$), 2.58 and 2.62 (2 overlapping d, 2, J = 7–8 Hz, $CH_2C=O$), 3.3 (m, 1, methinyl H), 4.05 and 4.15 (2 overlapping q, 4, J = 6–7 Hz, 2 OCH_2CH_3), 6.81 (q, 1, vinyl H); mass spectrum *m/e* (rel intensity) 228 (7, M^+), 183 (90, M − C_2H_5O), 182 (93), 155 (21), 154 (100), 140 (18), 126 (57), 125 (20), 113 (27), 112 (27), 95 (27), 81 (33), 69 (22), 67 (39), 53 (16).

Saponification of **7** gave **2-ethylidene-3-methylglutaric acid** as needles from benzene–hexane, mp 129–130° (lit.[16] mp 129°).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.79; H, 7.09.

From chromatographic effluent d was isolated **4d** (31%).

When this electroreduction experiment was repeated in exactly the same way except that the ethyl crotonate was only stirred with the catholyte (open circuit) for 23 min after reduction of **1d** (alone) was complete, there resulted **4d** (25%) but no **7**.

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Registry No.—**1a**, 4192-77-2; **1b**, 29584-63-2; **1c**, 40918-86-3; **1d**, 24393-65-5; **1e**, 40918-88-5; **1f**, 24393-66-6; **1g**, 40918-96-5; **1h**, 40918-97-6; **1i**, 40918-98-7; **1j**, 29584-64-3; **2**, 623-70-1; **3**, 40918-90-9; **4a**, 40918-91-0; **4c**, 40918-92-1; **4d**, 41021-30-1; **4g**, 40918-93-2; **4h**, 40918-94-3; **4i**, 40918-95-4; **4j**, 40919-00-4; **5**, 40919-01-5; **6**, 13351-28-5; **7**, 18418-07-0; **10**, 5462-13-5; benzylamine, 100-46-9; *N*-benzyl-3-(3,4-dimethoxyphenyl)-propionamide, 40958-49-4; 2-ethylidene-3-methylglutaric acid, 40919-04-8.

Condensation–Cyclization Reactions of Electron-Deficient Aromatics. VII. The Kinetics and Mechanism of Carbanionic σ-Complex Formation and Cyclization

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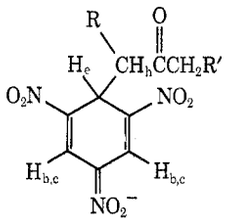
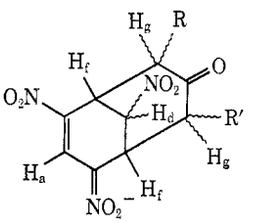
The kinetics and mechanism of formation and cyclization of the anionic σ complex obtained from the reaction of *sym*-trinitrobenzene and dibenzyl ketone are described. The reaction sequence is likely typical of a variety of similar condensation–cyclization reactions of electron-deficient aromatics with carbanions. Very rapid formation of anionic σ complex is followed by slow cyclization to bicyclic nitropropene nitronate.

Anionic σ complexes have been the subject of numerous thermodynamic and kinetic studies, both as metastable intermediates in aromatic nucleophilic substitution reactions and as products of aromatic addition. Much of this work has been summarized in several reviews.[1–5] The factors which govern the stability of such species and the way in which they are formed are now well known for a variety of different systems. In addition, the recently reported kinetic characterization of an observable metastable anionic σ complex intermediate in aromatic nucleophilic substitution in the naphthalene series[6] substantiates many early steady-state kinetic studies which had provided evidence for similar intermediates.[7–9] The resurgent interest in thermodynamic and kinetic characterizations of σ complexes of a variety of organic and inorganic bases with electron-deficient aromatics has provided considerable evidence substantiating the structure of these species and the way in which they form and decompose.

During the past 4 years, it has become clear that many carbanionic σ complexes, **1**, are unstable, not with regard to formation of a substitution product (which would require hydride expulsion), but because they readily undergo an internal cyclization reaction to yield the stable bicyclic nitropropene nitronate salts, **2**.[10–21]



1a, R = R′ = C_6H_5
b, R = R′ = -(CH_2CH_2)-
c, R = R′ = CH_3
d, R = R′ = H



2a, R = R′ = C_6H_5 (trans)
b, R = R′ = C_6H_5 (cis-endo)
c, R = R′ = C_6H_5 (cis-exo)

Isolation of intermediates, as well as qualitative visible and pmr spectral studies of the reaction, has provided evidence for two distinct cyclization mecha-

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