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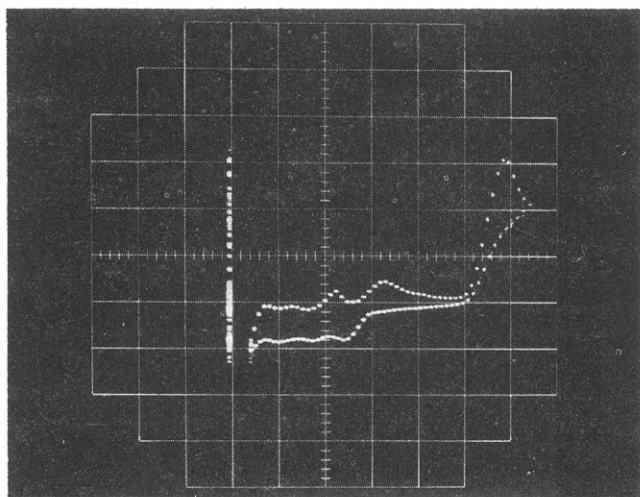Figure 1.—Methyl tosylate: continuous sweep cyclic voltammetric curve for ~10 mM MeOTs in 0.10 M Pr₄NClO₄–MeCN. Signal oriented with reduction current (300 μA/cm) up and cathodic potential (0.5 V/cm) to the right. The irregular line 2 cm to the left of center denotes zero on the potential axis.
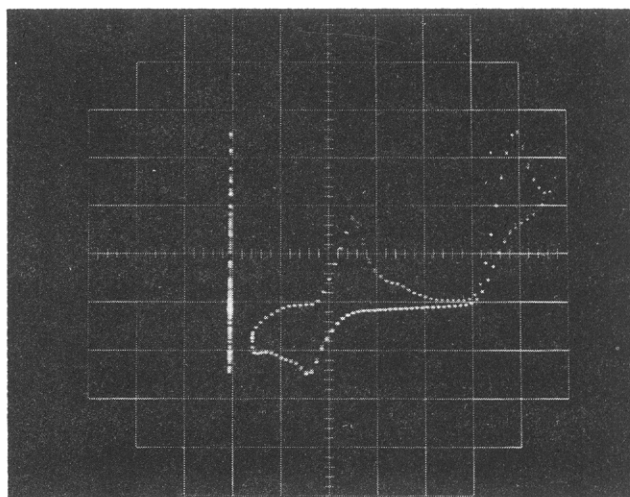


Figure 2.—Methyl tosylate with methanol: conditions as described in the caption of Figure 1.



Figure 3.—Methyl tosylate with methanol and phenol: conditions as described in the caption of Figure 1.

in one experiment with dimethylformamide. Tetraethylammonium bromide, tetrapropylammonium iodide, and tetrapropylammonium perchlorate were used as supporting electrolytes. Coulometry and product analysis results are presented in Table II. With carbon electrode reductions, reaction current dropped continuously to the background. Initial currents were typically 25–30 mA, final currents typically 0.1–0.2 mA. With mercury cathodes, the initial current was about as indicated; however, instead of dropping continuously, the current went through a maximum, typically a few milliamperes above the starting value, a few minutes after the start of the reaction. It then fell rapidly to the background value.

TABLE II

CONSTANT POTENTIAL REDUCTION OF ALKYL TOSYLATES

at −2.80 V vs. Ag–AgNO₃

| Compound | Working electrode | Supporting electrolyte | $n^a$ | % $ROH^b$ | % ROR | % PhCH₃ |
|---|---|---|---|---|---|---|
| Methyl | C | TPAP$^c$ | 1.0 | 24 | 36 | 27 |
| tosylate | Hg | TPAP | 1.0 | 44 | ... | 25 |
| | Hg | TEAB$^d$ | 1.0 | 42 | | |
| Ethyl | C | TPAP | 1.1 | 32 | 35 | 30 |
| tosylate | | | | | | |
| n-Butyl | C | TPAP | 1.0 | 62 | 18 | 26 |
| tosylate | Hg | TPAP | 1.1 | 58 | ... | 28 |
| Neopentyl | C | TPAP | 1.2 | 68 | | 34 |
| tosylate | C | TPAI$^e$ | 1.4 | 98 | ... | 28 |
| | Hg | TPAI | 1.3 | 97 | ... | 25 |
| Cyclohexyl | C | TPAP | 1.2 | 75$^f$ | ... | 4 |
| tosylate | Hg | TPAP | 0.91 | 60$^g$ | ... | 23 |
| | C | TEAB | 2.0 | 96 | ... | Trace |
| | Hg | TEAB | 1.9 | 96 | ... | Trace |

$^a$ Number of electrons per molecule of starting tosylate. $^b$ All yields mole % of starting tosylate. $^c$ Tetra-n-propylammonium perchlorate. $^d$ Tetraethylammonium bromide. $^e$ Tetra-n-propylammonium iodide. $^f$ Plus 4% cyclohexanone. $^g$ Plus 5% cyclohexanone.

In addition to the compounds indicated in Table II, others were identified, but not quantitatively determined, in the reaction mixture. Propylene and tripropylamine were identified as products of reactions for which tetrapropylammonium ion was used as sup-
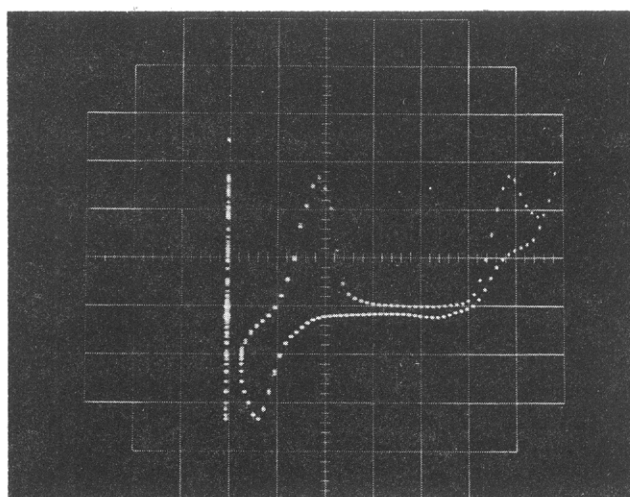
porting electrolyte. Alkanes corresponding to the alkyl group of the tosylate being examined were sought unsuccessfully.

Toluene and sulfinate anions were identified by ultraviolet absorption spectroscopy. The volatile fraction of the contents of the cathode compartment was removed at reduced pressure and trapped at liquid nitrogen temperature. The ultraviolet spectrum of the volatile fraction was identical with that of toluene. The residual solid was taken up in water. This solution showed absorption peaks at 220 and 260 mμ. After acidifying, the 220-mμ peak was changed, the 260-mμ peak was eliminated, and a more intense peak was observed at 240 mμ. The Sadtler Standard ultraviolet spectrum collection shows, for p-toluenesulfinate in methanol, peaks at 268, 263–265, and 222 mμ, with extinction coefficients of 999, 969, and 12,200, respectively. After acidifying, the peaks are shown at 241 and 222 mμ, with extinction coefficients of 3310 and 11,400, respectively. This behavior was observed for products of mercury cathode reduction of methyl, butyl, and cyclohexyl tosylates and for carbon electrode reduction of cyclohexyl tosylate. It is assumed that it would be observed in all cases and that it constitutes a qualitative indication of the presence of p-
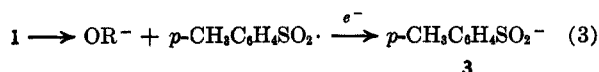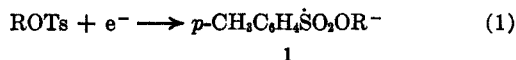
toluenesulfinate anion in the products. $p$-Toluenesulfonate ion shows ultraviolet absorption at 221 m$\mu$, unaffected by acid. Since this is at nearly the same wavelength as the similarly unaffected peak of $p$-toluenesulfinate ion, the presence of sulfonate cannot be proved or disproved on this basis.

There was no indication, by gas chromatography or ultraviolet spectroscopy, that any unidentified compounds in significant amounts were present.

Attempts were made to detect mercury in the reaction mixtures by atomic absorption spectroscopy. These were unsuccessful because of the large signal caused by the solvent. Volatile components of the product mixtures were removed under reduced pressure, and the determination was repeated on carbon tetrachloride extracts of the remaining solids. No mercury was detected. Standard sample determinations indicated that mercury in excess of 1 mol % of the starting tosylate should have been detected by this procedure; however, volatile compounds would not have been found.

### Discussion

The electrolytic reduction of tosylates has been carried out at carbon and mercury electrodes. A scheme for the reaction at the carbon electrode is outlined in eq 1 through 7 below. It is suggested that the

$$\text{ROTs} + e^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\overset{.}{\text{S}}\text{O}_2\text{OR}^- \quad (1)$$
$$\mathbf{1}$$

$$\mathbf{1} \longrightarrow \text{ROSO}_2^- + \text{CH}_3\langle\bigcirc\rangle\cdot \xrightarrow{e^-} \text{CH}_3\langle\bigcirc\rangle^- \quad (2)$$
$$\mathbf{2}$$

$$\mathbf{1} \longrightarrow \text{OR}^- + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\cdot \xrightarrow{e^-} p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2^- \quad (3)$$
$$\mathbf{3}$$

$$\mathbf{2} + \text{H}^+ \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 \quad (4)$$

$$\text{RO}^- + \text{H}^+ \longrightarrow \text{ROH} \quad (5)$$

$$\text{RO}^- + \text{ROTs} \longrightarrow \text{ROR} + \text{OTs}^- \quad (6)$$

$$\text{ROSO}_2^- + \text{H}_2\text{O} \longrightarrow \text{ROH} + \text{HSO}_3^-\cdot \quad (7)$$

initial step involves addition of one electron to the tosylate forming a very short-lived anion radical having the unpaired electron localized at the sulfur atom. This is based on our failure to observe any indication of reversibility, indicating radical lifetimes of less than a few milliseconds. This anion radical could decompose by scission of either a carbon–sulfur bond as in step 2 or a carbon–oxygen bond as in step 3. It is suggested that at the potential required for step 1, the $p$-tolyl radical produced by decomposition of $\mathbf{1}$ is immediately reduced to the $p$-tolyl carbanion, $\mathbf{2}$. Protonation of $\mathbf{2}$ in step 4 would account for the appearance of toluene as a product.

Cleavage of a sulfur–oxygen bond in the decomposition of $\mathbf{1}$ yields alkoxide ions and $p$-toluenesulfinyl radicals which are presumably immediately reduced to sulfinate ions, as indicated in step 3. The formation of $\mathbf{3}$ is inferred from the ultraviolet data. Since only one reduction peak is observed in the cyclic voltammetric curve, immediate reduction of the radical seems indicated.

The recovery of substantial yields of alcohols reflects protonation of alkoxide during or after the electrolysis. Identification of propylene and of tripropylamine indicates that the supporting electrolyte is serving as at least a partial source of protons for steps 4 and 5. A possible reaction is shown in eq 8. Quantitative

$$\text{R}^- + \text{Pr}_4\text{N}^+ \longrightarrow \text{RH} + \text{CH}_3\text{CH}{=}\text{CH}_2 + \text{Pr}_3\text{N} \quad (8)$$
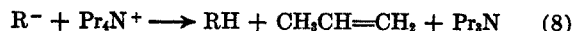
studies in connection with other work show that an analogous reaction of tetraalkylammonium ions could account for only a part of the protons involved. The remainder were shown to come from the solvent, acetonitrile.[4] It is likely that the same is probably true in these experiments.

Isolation of substantial yields of ethers suggests the displacement reaction indicated in step 6. The reaction of alkoxides with tosylates has been studied and shown to involve an S$_N$2 displacement.[5] The yields of ethers indicated in Table II decrease in the order methyl > ethyl > butyl > neopentyl, as would be expected for an S$_N$2 reaction.

The results obtained for carbon cathode large-scale reductions are reasonably compatible with the reaction scheme proposed. The major discrepancy is failure to account for all of the alkyl groups of the starting tosylate sample in the reaction of neopentyl and cyclohexyl tosylates. It may be noted that use of halide salts, rather than perchlorates, resulted in a nearly quantitative recovery of alcohols in these cases.

Reactions at mercury cathodes differed from those at carbon cathodes in that no ethers were formed from methyl or butyl tosylates. This evidently indicates that alkoxide ions are prevented from coming in contact with unreacted tosylate, since it is known that ethers are formed under the conditions of these experiments. The possibility was considered that the absence of ethers simply indicates that, at mercury electrodes, step 3 is not occurring. Alcohol and toluene would be produced by steps 2, 4, and 7. This, however, would require the formation of equal amounts of alcohol and toluene. Since the yields of alcohols are much larger than yields of toluene, step 3 cannot be omitted. It may be possible that the composition of the electrical double layer at the mercury–solution interface, which would be expected to differ from the double layer at a carbon–solution interface, is responsible for this difference.

The possibility that formation of unreactive organomercury compounds may be responsible for failure to account for all of the alkyl groups in the reduction of low-molecular-weight tosylates at mercury cathodes was considered. An attempt was made to detect mercury in butyl tosylate reaction products by atomic absorption spectroscopy. Direct determination on the reaction mixture was unsuccessful because of the large background signal caused by the solvent. Removal of the solvent followed by analysis of extracts of the residual solids gave negative results. This does not eliminate the possibility of an unreactive volatile mercury compound having been formed.

(4) C. K. Mann, J. F. Webb, and H. M. Walborsky, *Tetrahedron Lett.*, 2249 (1966); additional data to be published.

(5) C. H. Snyder and A. R. Soto, *J. Org. Chem.*, **29**, 742 (1964).

**Cyclic Voltammetry.**—We suggest that the A voltammetric peak is caused by the electron-transfer reactions in steps 1, 2, and 3 of the proposed scheme for all compounds studied. This assignment is made because the constant potential reductions, carried out at the potential of the A peak, produced products which could be formed from these reactions and because only one reduction peak occurred at this potential.

It is evident from Figure 2 that addition of methanol eliminates the B–C pair and augments the pair immediately to the left. We attribute this to reaction 9 which forms methoxide.

$$CH_3\langle\bigcirc\rangle^- + MeOH \longrightarrow PhCH_3 + MeO^- \qquad (9)$$
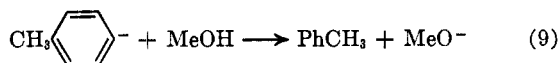
Addition of potassium methoxide to a solution such as that being electrolyzed to obtain Figure 2 causes an increase in the peaks attributed to methoxide without causing other changes, except for the appearance of a pair of reversible peaks due to the potassium couple.

Addition of phenol to the solution illustrated in Figure 2 produces the solution electrolyzed to get Figure 3. The methoxide peaks are eliminated and a pair of peaks at more anodic potentials is generated. These coincide with phenoxide peak potentials. Presumably phenol is protonating methoxide.

These results show that, for methyl tosylate, methanol eliminates the B peak reactant and that, as expected from the $pK_a$ values in Table III,[6] phenol removes both the B peak reactant and methoxide.
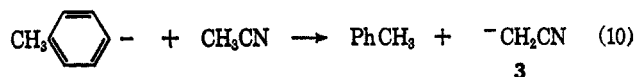
TABLE III[6]

| Compound | $pK_a$ |
|---|---|
| Phenol | 10 |
| Methanol | 16 |
| Ethanol | 18 |
| Acetonitrile | 25 |
| Benzene | 37 |

It has been noted with amines that a correlation exists between base strength and ease of oxidation of the base. Values of $pK_a$[7] and cyclic voltammetric oxidation peak potentials[8] have both been shown to be correlated with polar substituent constants for substituents on the nitrogen atoms. Potentials can therefore be correlated with $pK_a$ values. The stronger the base, the more easily it is oxidized. This would be anticipated considering the Lewis definition of a base.

We have observed that the order of increasing ease of oxidation of the conjugate bases of phenol, and the alcohols examined is phenoxide < methoxide < ethoxide < cyclohexoxide, with cyclohexoxide most easily oxidized. We base this on observations of the effect of successive addition of alkali alkoxides and alcohols to a solution while a voltammetric signal is being observed. This type of experiment is not suited to quantitative measurement of potentials, but as can be seen from Figures 2 and 3 does give unequivocal qualitative information. Again, the stronger the base, the more easily it is oxidized.

Regarding the identity of the reactant being oxidized at the B peak, one possibility is the tolyl carbanion 2

formed in step 2 of the reaction scheme. Another possibility is cyanomethylene carbanion 3 formed in eq 10.

$$CH_3\langle\bigcirc\rangle^- + CH_3CN \longrightarrow PhCH_3 + {}^-CH_2CN \qquad (10)$$
$$\mathbf{3}$$

From the $pK_a$ values in Table III, it would be expected that step 10 would occur, if it is accepted that the $pK_a$ of toluene for the loss of the *para* hydrogen would be about the same as that of benzene. The potentials given in Table I for the B peaks are, within experimental error, the same for all compounds examined. This would be the case for either alternative. We suggest that the correlation between bacisity and oxidation potential should be valid for carbanions as well as amines and alkoxides. If so, then the potential for oxidation of 2 would be more cathodic than for oxidation of 3 which would, in turn, be more cathodic than the methoxide oxidation peak.

On the basis of the data presently available, we cannot definitely distinguish between then two possibilities. We are inclined to believe that the B peak is caused by oxidation of 2 and that, although reaction 10 is occurring, we are seeing that fraction of 2 formed at peak A which survives the 0.2-sec period which elapses between peak A and peak B. This could be adsorbed on the microelectrode. As one indication that this may be true, we have seen, in other work,[4] peaks which can reasonably be ascribed to alkyl and aryl carbanions produced by electrochemical reduction of alkyl and aryl halides which occurred near but not at the potential of the B peaks. A peak which behaved like the B peak was observed on reduction of *m*-bromotoluene. If 2 is entirely eliminated in favor of 3, then presumably the same would be true for other carbanions, since they are, in general, substantially more basic than 3. It may be noted that the methoxide peaks in Figure 2 are substantially larger than the B peaks of Figure 1. This suggests that we are seeing in Figure 1 the oxidation peak of the surviving portion of 2, followed by the oxidation of the 3 formed and of methoxide. This results in the fairly substantial but varying current indicated to the left of the B peak in Figure 1. When methanol is added, it protonates all of 2 and 3, leaving a single much larger methoxide peak in Figure 2.

The cyclic voltammetry curve was obtained for methyl tosylate in dimethylformamide solutions. It was qualitatively similar to that obtained in acetonitrile. This observation is in accord with our supposition that the B peak is due to 2, since it leads us to expect that the solvent change should not eliminate the B peak. However, this does not prove the point either way since a reaction of 2 with dimethylformamide to form an oxidizable substance is possible.

The other tosylates studied are derivatives of more weakly acidic alcohols than methanol. This is reflected in a rather ill-defined B peak for ethyl and butyl tosylates, presumably because the alkoxide oxidation is occurring at only slightly less anodic potentials than are required for the B peak.

The case of cyclohexyl tosylate is different from the others in one respect. The B peak for this compound is large and well defined; however, investigation showed that this is caused by the coincidence of cyclo-

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 1.

(7) H. K. Hall, *J. Amer. Chem. Soc.*, **79**, 5441 (1957).

(8) C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964).

hexoxide being oxidized at very nearly the same potential as is required for 2 or 3. Addition of cyclohexanol to a solution of the tosylate did not eliminate the B peak, in contrast to the effect of methanol on the B peak of methyl tosylate. Instead, there was a very slight shift of peak potential in the anodic direction, indicative of the slightly less cathodic oxidation potential of cyclohexoxide as compared with that of 2 or 3. Addition of cyclohexoxide caused the B peak to increase without affecting the rest of the signal. Addition of methanol eliminated the cyclohexoxide peak, as expected.

The authors intend to investigate further the behavior of very easily oxidized anions. However, they expect to use a system other than tosylate because the mixture of products produced causes undesirable voltammetric complexity.

### Experimental Section

**Reagents.**—Acetonitrile was prepared according to the procedure previously described.[9] Commercial tetraethylammonium bromide was recrystallized from methanol and dried under a vacuum at 80°. Tetrapropylammonium perchlorate was prepared from the iodide as previously described by Kolthoff.[10]

Methyl, ethyl, neopentyl, and cyclohexyl tosylates were prepared according to the procedure of Tipson.[11] Our experimental melting points agreed with literature values for the following: cyclohexyl tosylate, 44°: methyl tosylate, 28°; ethyl tosylate, 32°;[12] neopentyl tosylate, 48°.[13] *n*-Butyl tosylate was Eastman White Label.

(9) J. F. O'Donnell, J. T. Ayers, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

(10) I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 870 (1957).

(11) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(12) R. S. Tipson, M. A. Clapp, and L. H. Cretchen, *ibid.*, **12**, 133 (1947).

(13) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

Dicyclohexyl ether, with a boiling point of 244° (lit.[14] bp 239–240°), was prepared by a hydrogen–Raney nickel reduction of phenylcyclohexyl ether in cyclohexane solution at 175° and 30 atm. Other reagents were the best available grade, used without purification.

**Cyclic Voltammetry.**—Cyclic voltammetry curves were obtained on the apparatus previously described.[15] Sweep rates were 10 V/sec, with a 3-m/sec step width. The microelectrode was a mercury-plated platinum wire. A silver–0.10 *M* AgNO₃-acetonitrile reference electrode was used for all electrolyses. Voltammetric curves were recorded using unthermostated cells in a room having ambient temperature at 22°.

**Constant Potential Electrolyses.**—Electrolyses were performed with a conventional three-electrode potentiostat. All electrolysis cells were constructed to permit use of vacuum-line techniques for solution handling. Large-scale electrolyses were performed in H cells with either mercury pool or glassy carbon cathodes and silver or platinum anodes. Solutions were degassed by repeated freezing and pumping and were then stored under a nitrogen or a helium atmosphere.

**Product Analyses.**—Reaction vessels were fitted with septums which allowed direct sampling of cathode solution or head space by a syringe. Alcohols, ethers, tripropylamine, propylene, methane, ethane, butane, cyclohexane, neopentane, and toluene were determined or sought by gas chromatography, on appropriate columns, on samples taken directly from the cathode compartment. In all cases, valid samples of compounds of interest were chromatographed for comparison. This applies also to compounds sought but not found, *e.g.*, methane after methyl tosylate reduction; care was taken to ascertain that these would be seen, if present, considering the interferences present in the samples analyzed.

Toluene and *p*-toluenesulfinate ion were detected by ultraviolet absorption spectroscopy.

Mercury analyses were performed on reaction mixtures with a Perkin-Elmer Model 290 atomic absorption spectrometer.

(14) H. Willstatler, *Chem. Ber.*, **45**, 1466 (1912).

(15) C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964).

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# The Tetramers of Acetylenedicarboxylic Esters[1]

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Dimethyl and diethyl acetylenedicarboxylate form thermal tetramers which have been characterized as cyclopropenyl derivatives of oxanorbornadiene 1a and 1b. Various degradative reactions verify this structural assignment. The hexadeuterated tetramer analog 1c was synthesized by trapping the reactive cyclopropenylfuran 10a with dimethyl acetylenedicarboxylate-*d₆*. The tetramer of the methyl ester undergoes photochemical reaction to form semibullvalene derivative 13.

The dimethyl[2,3] and diethyl esters of acetylenedicarboxylic acid spontaneously react to form tetrameric products. From spectral studies Le Goff and LaCount have recently proposed the cyclopropenyloxanorbornadiene structure 1a for the crystalline methyl ester 1a.[3] The chemical and spectral studies here reported verify this assignment. The tetrameric ethyl ester which exhibits similar infrared and ultraviolet spectra is assigned analogous structure 1b.

**Spectral Features.**—The tetramers and several of their derivatives described below exhibit medium
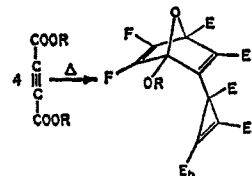


1a, E = F = COOCH₃; R = CH₃
b, E = F = COOC₂H₅; R = C₂H₅
c, E = COOCH₃; F = COOCD₃; R = CH₃

intensity absorptions at 1870–1900 cm⁻¹ in their infrared and Raman spectra. Absorptions in this region are characteristic of the highly substituted cyclopropene ring system,[4] although compounds containing conju-

(1) Presented in part at the Third Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968.

(2) (a) M. J. Goldstein, private communication. (b) G. L. Thayer, Jr., Thesis, Cornell University, 1965, p 89 ff; *Dissertation Abstr.*, **26**, 104 (1965).

(3) E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2333 (1967).

(4) (a) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 74 (1966); (b) *ibid.*, **1**, 115 (1966).