in the syringe and injected into 3.00 mL of an aqueous solution containing 0.0091 N HCl and 0.017 M KCl. The temperature of the solution was maintained at 60 °C by using a water bath, and the procedure was performed inside an enclosure containing a nitrogen atmosphere. Another aqueous solution was prepared which contained 0.02 M Tris in the free base form, and 2×10^{-5} M 1. After equal volumes of these two solutions were mixed in the stopped-flow spectrophotometer, the final pH was measured as 7.50. After correction for a 0.025-mL holdup in the injection syringe, the final concentration of 2 was calculated to be 5.02×10^{-4} M and that of 3 to be 5.00×10^{-4} M. In all experiments, the ionic strength of the mixed solution was calculated to be 0.01 ± 0.003, disregarding the contribution of the surfactant to the ionic strength.

Kinetic Studies. Reactions were monitored with a Durrum Model D-130 stopped-flow spectrophotometer equipped with a Beckmann Model DU-2 monochromater and a Tektronix Model 5103N/D15 storage oscilloscope. The oscilloscope readout was photographed by using a Polaroid camera. A constant-temperature circulating bath maintained the temperature at 25 ± 0.2 °C. The appearance of the EllS$^-$ product was followed at 445 nm.[13b] All reactions were monitored with two oscilloscope time bases, one appropriate to the faster reactions and one appropriate to the slower reactions. Rate constants were calculated from the appropriate traces. First-order kinetic behavior was observed for the fastest reaction, with correlation coefficients greater than 0.999 for computer-generated correlations of log $(A_1^\infty - A^t)$ with time. The fastest reaction was rapid enough so that product oxidation could be ignored.

The rate of the second reaction in Scheme I was in all cases comparable to the rate of product oxidation. The relative rate constants for the second reaction were therefore calculated from the maximum product concentrations observed. The relative maximum concentration from the second step, β_{max}, was obtained by subtracting from the maximum observed concentration that amount of product that was due to the first step (1×10^{-5} M) and then dividing the result by the theoretical total product yield from the second step (also 1×10^{-5} M). If $k_{\psi 2}$ is the pseudo-first-order rate constant for the second step in Scheme I and k_{ox} is the pseudo-first-order rate constant for product oxidation, then β_{max} can be approximated by $(k_{ox}/k_{\psi 2})$ raised to the power $k_{ox}/(k_{\psi 2} - k_{ox})$.[22] The ratio between $k_{\psi 2}$ and k_{ox} was then calculated for β_{max} in each case. On the assumption that k_{ox} was the same in each case, the "ratio of ratios" thus gave the relative rate constants for the second step at different thiol concentrations.[23]

The estimate of k_2 was obtained from measurement of the time at which β_{max} was observed, τ_{max} in the experiment with 0.001 M 2. By use of the above rate constants, τ_{max} can be approximated by $(1/(k_{ox} - k_{\psi 2}))\ \ln\ (k_{ox}/k_{\psi 2})$.[22] The nature of the absorption vs. time reaction trace was such that a precise τ_{max} value was not obtained; nevertheless τ_{max} lay between 10 and 100 s. Using these two boundary τ_{max} values and the relation $k_{ox} = 0.138\ k_{\psi 2}$ (from the β_{max} value), we calculated that $0.0032\ s^{-1} < k_{\psi 2} < 0.032\ s^{-1}$; we thus estimate that $k_2 < 32\ L\ mol^{-1}\ s^{-1}$.

The occurrence of the oxidation reaction, which forces us to resort to the foregoing analysis, cannot be easily prevented. The vesicles were prepared in a nitrogen atmosphere, but oxygen is apparently introduced during the transfer of the solutions to the stopped-flow spectrophotometer. We suspect that only be enclosing that instrument in a nitrogen atmosphere, and thus performing the *entire* experiment under an inert atmosphere, could we completely eliminate the complication of product oxidation.

Acknowledgment. I thank Professor Robert A. Moss for helpful discussions and Professor Jean-Marie Lehn for assistance in preparing this paper. Financial support from the National Science Foundation is also gratefully acknowledged.

Registry No. 1, 69-78-3; 2, 79246-00-7; 3, 70755-47-4; $(n\text{-}C_{16}H_{33})_2N^+(CH_3)CH_2CH_2SSEll$, 85908-82-3.

(22) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism", 3rd ed.; Wiley: New York, 1981; p 290 ff.

(23) It must be noted that this is a crude calculation; the relations used are exactly true only for two consecutive first-order reactions. The system we observed involved two parallel pseudo-first-order reactions, followed by a third, consecutive pseudo-first-order reaction. There is no simple kinetic solution which can analyze completely such a system. Therefore, the initial reaction has been ignored, because it is much more rapid than the two reactions which follow.

Diels–Alder Reactions of 2-Alkynoyl Chlorides with Cyclopentadiene: A Reinvestigation

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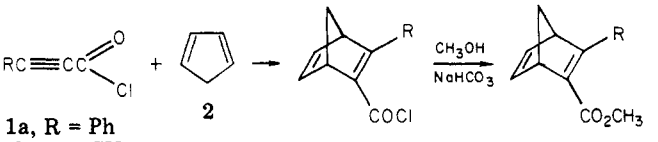
Diels–Alder reactions of cyclopentadiene represent a simple access to the bicyclo[2.2.1] skeleton.[1a] While electron-deficient alkenes react readily with cyclopentadiene,[1b,c] cycloadditions to triple bonds appear to be problematic.

While alkenoyl chlorides are among the most reactive dienophiles,[1b,c] phenylpropynoyl chloride has been reported "not to undergo appreciable reaction with cyclopentadiene at room temperature even after 24 h".[2] Therefore, Baum and Viehe used a route via acetylenic iminium salts for synthesizing compounds of type 4.[3] In earlier papers, however, Diels–Alder reactions of **1a** with cyclopentadiene have been reported.[4,5] Forty-one percent of cycloadduct was obtained when a solution of **1a** and 2 in toluene was heated at reflux for 48 h.[4] Other workers describe a spontaneous reaction of **1a** with 2 at room temperature in the presence of a "few crystals of picric acid".[5] The inconsistency of these reports prompted us to reexamine the reactions of alkynoyl chlorides with cyclopentadiene.

When **1a** and 2 were mixed at 0 °C, warmed up to room temperature, and poured into a suspension of sodium bicarbonate in methanol, 84% of ester **4a** was obtained. Combining these cycloaddends without external cooling resulted in a rapid exothermic cycloaddition reaction accompanied by partial polymerization of cyclopentadiene. Alkynoyl chlorides **1b** and **1c** reacted with cyclopentadiene at room temperature to give good yields of norbornadienes **4b** and **4c**, respectively. Because of the mild reaction



1a, R = Ph
b, R = CH_3
c, R = $C(CH_3)_3$

4a, 84%
b, 78%
c, 82%

conditions employed for these cycloadditions[6] and the versatile reactivity of acid chlorides 3, we consider the title reaction as the method of choice for the synthesis of any

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norbornadiene-2-carboxylic acid derivatives. Since even the sterically hindered tertiary butyl compound **1c** reacts readily at room temperature, this reaction should be of general applicability.

Experimental Section

General Procedures. Infrared spectra were recorded on a Beckman Acculab 1 IR spectrophotometer. ^1H NMR spectra were taken in carbon tetrachloride on a JEOL JNM-C-60-HL spectrometer, and mass spectra were recorded on a Varian MAT CH 4 spectrometer.

Methyl 3-Phenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (4a). Cyclopentadiene (2.70 g, 40.9 mmol) was added to precooled (0 °C) phenylpropynoyl chloride (**1a**;[7] 6.00 g, 36.5 mmol) in a nitrogen atmosphere and the mixture was allowed to warm to 20 °C within 4 h. After 10 h, more cyclopentadiene (2.70 g, 40.9 mmol) was added. After the mixture was stirred for 24 h, **1a** was consumed completely (monitoring by NMR) and the mixture was added slowly to a suspension of $NaHCO_3$ (3.5 g) in 50 mL of methanol. After 1 h, the mixture was filtered and the solvent evaporated. The residue was dissolved in 20 mL of ether and filtered, the ether evaporated, and the residue distilled: 6.93 g (84%) of **4a**; bp 109–110 °C (0.2 mmHg) [lit.[4] bp 111–116 °C (0.6 mmHg)]; IR (neat) 3050, 2980, 2940, 2870, 1705, 1605, 1590, 1485, 1425, 1330, 1290, 1230, 1185, 1145, 1095, 1080, 1070, 755, 715, 690 cm^{-1}; ^1H NMR (CCl_4) δ 2.03, 2.23 (br AB system, J = 7 Hz, 2 H), 3.60 (s, 1 H), 3.82 (br s, 1 H), 4.03 (br s, 1 H), 6.94 (br s, 2 H), 7.1–7.7 (m, 5 H); mass spectrum (70 eV), m/e (relative intensity) 226 (100, M^+), 195 (24), 167 (63), 166 (21), 165 (39), 161 (69), 152 (15), 129 (47).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.50; H, 5.96.

Methyl 3-Methylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (4b). 2-Butynoyl chloride (**1b**; from 2-butynoic acid[8] and $SOCl_2$;[9] 4.00 g, 39.0 mmol) and cyclopentadiene (2.70 g, 40.9 mmol) were combined at room temperature (N_2 atmosphere). After 48 h at ambient temperature more cyclopentadiene (2.70 g, 40.9 mmol) was added, and the mixture was left for another 48 h and worked up as above. The crude material was purified by filtration over silica gel. After elution of dicyclopentadiene with petroleum ether, **4b** was eluted with ether, the ether evaporated, and the residue distilled: 5.0 g (78%) of **4b**; bp 67–70 °C (4 mmHg) [lit.[6] bp 85–90 °C (15 mmHg)]. For spectral data, see ref. 6.

Methyl 3-*tert*-Butylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (4c). 4,4-Dimethyl-2-pentynoyl chloride (**1c**; from 4,4-dimethyl-2-pentynoic acid[10] and $SOCl_2$;[9] 9.00 g, 62.2 mmol) and cyclopentadiene (5.00 g, 75.6 mmol) were combined at 20 °C (N_2 atmosphere). After 30 h more cyclopentadiene (4.10 g, 62.0 mmol) was added, and the mixture was stirred for 5 days at room temperature and worked up as described for **4a**: 10.5 g (82 %) of **4c**; bp 62–64.5 °C (1 mmHg); IR (neat) 3070, 2950, 2870, 1720, 1600, 1560, 1480, 1460, 1435, 1365, 1300, 1235, 1195, 1160, 1090, 1050, 725 cm^{-1}; ^1H NMR (CCl_4) δ 1.16 (s, 9 H), 1.88 (m, 2 H), 3.67 (s and m, 5 H), 6.82 (m, 2 H); mass spectrum (70 eV), m/e (relative intensity) 206 (58, M^+), 191 (21), 175 (22), 174 (40), 159 (24), 147 (80), 141 (51), 131 (100).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 76.00; H, 9.05.

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Registry No. **1a**, 7299-58-3; **1b**, 39753-54-3; **1c**, 52324-03-5; **4a**, 24161-43-1; **4b**, 85894-25-3; **4c**, 85894-26-4; cyclopentadiene, 542-92-7.

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Sulfinic Acids and Related Compounds. 14. Derivatives of 3-Sulfinopropanoic Acid[1,2]

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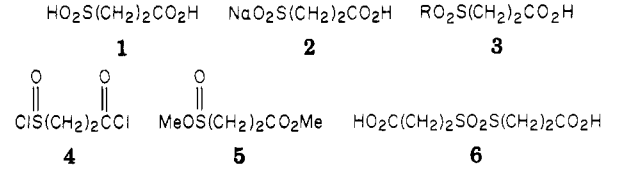
Sulfinate salts containing di- or trisulfide linkages have shown promise as antiradiation drugs.[3] An attractive alternative to long sequential syntheses of such structures would be convergent syntheses in which separately synthesized sulfinic acid derivatives and di- or trisulfides become connected by a carboxylate ester linkage involving CO_2H on one of the synthons and OH on the other. For such purposes, 3-sulfinopropanoic acid (**1**), as its sulfinate salt (**2**) or ester (**3**), is an attractive synthon both per se and as a model. This paper reports studies of several compounds related to **1**: the salt **2**, the diacid dichloride **4**, the diester **5**, the thiolsulfonate **6**, and various related compounds.



A reported method for oxidizing thiols to sulfinic acids, in which *m*-chlorobenzoic acid precipitates,[6] was unsatisfactory with 3-mercaptopropanoic acid (**7**) because **1** coprecipitated. However, when an alkaline solution of the products was adjusted to pH 3, the acid **1** (pK_a probably of ~2 for SO_2H)[7] remained in solution as its salt, while *m*-chlorobenzoic acid could be extracted (pK_a = 3.8,[8] sparingly soluble). The spectra of **2** obtained by evaporating the aqueous phase met expectation and showed a negligible amount of *m*-chlorobenzoic acid. Titration for sulfinic acid content by the method of Marvel and Johnson, by using nitrous acid,[9] indicated a content in the salt **2** of ~94% of sulfinate (with allowance for NaCl, which could not readily be separated and usually would be inconsequential); this titration is selective for sulfinic acids in the presence of sulfonic or carboxylic acids and related materials.[9b] The identity of the **2** was confirmed by conversion to a bis(benzylthiuronium) salt. Efforts to condense the carboxy salt **2** with bis(2-hydroxyethyl) disulfide have been unpromising so far because of solubility problems,[2] however, and we therefore turned to a study of the diacid dichloride **4**.

Douglass and Farah prepared **4** by chlorinating the mercapto acid **7**,[10] and others also have encountered no

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