acids. In other work, very large values for the ratios of the ionization constants of diacids, K_1/K_2 , were explained by a stabilization of the monoanion by intramolecular hydrogen bonding and by an enhanced coulombic interaction in cases where the COO⁻ and COOH groups were held near one another.^{24,25} In a recent study on the thermodynamics of ionization of dicarboxvlic acids, Purdie and Tomson indicated some reservations about the hydrogen-bonding theory.²⁶ The ionization of several diacids was shown to be dominated by entropy effects, which suggests that solvation of the charged center(s) is of prime importance. "Cooperative solvation" of the COO⁻ and COOH groups by a set of solvent molecules was mentioned as a possible alternative to intramolecular hydrogen bonding in the monoanion. In phenylsuccinic acid (like succinic acid itself), the magnitudes and the differences between the first and second acid dissociation constants are closer to those of fumaric acid, in which the carboxylates are held remote from one another, than to those of maleic acid. Thus, neither conformation nor acidity of this particular molecule seems to be affected by intramolecular hydrogen bonding or cooperative solvation to any great extent. It is noteworthy, however, that the monoesters of phenylsuccinic acid are between two and four times less acidic than the diacid, and that the COOH group adjacent to phenyl is about two times more acidic than the other COOH group, perhaps owing to the inductive effect of phenyl.²⁷

In pyridine solution, the carboxylic acid groups are hydrogen bonded to solvent, but not ionized.²⁸ Significantly different nmr parameters result in this solvent: $J_{AB} = -16.8$, $J_{AX} = 5.2$, $J_{BX} = 9.9$, $J_{^{13}C-A} = 7.5$, and $J_{^{13}C-B} = 3.1$ Hz. These data suggest that conformer 2 is the dominant species in this solvent ($\sim 60\%$). The coupling constants in acetone- d_6 were quite similar to those in pyridine. Acetic acid- d_4 was tested to see if the coupling constants observed in this solvent would be similar to those found in aqueous solvents, since both are hydroxylic, or similar to the other organic solvents. As Table I indicates, all organic solvents are similar. Thus, the phenyl group prefers the least hindered position, trans to COOH, in the organic solvents tested, but the labeled COO⁻ group prefers the least hindered position in aqueous solvents.²⁹

¹³C spectra were obtained using the usual Fourier transform technique. The one-bond coupling constant between the labeled carbon and the carbon bearing phenyl was 55 Hz, approximately the same as that observed in acetic acid.³⁰ No splitting of the methylene

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(29) Intramolecular association of the carboxylates, similar to the wellknown acetic acid dimer, is quite unlikely owing to geometric restrictions. A single hydrogen bond between COOH groups could lead to a preference for conformer 2, although this is unlikely in the powerful hydrogen-bonding solvent pyridine. Carboxyl-phenyl association [cf. R. N. MacDonald and R. R. Reitz, J. Org. Chem., **37**, 2703 (1972), and H. S. ElKhadem, D. Horton, and T. F. Page, Jr., *ibid.*, **33**, 734 (1968)] would favor conformer 1, but its

presence in hydrogen-bonding solvents is also problematical. (30) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Reso-nance for Organic Chemists," Wiley, New York, N. Y., 1972, p 29.

carbon resonance was observed, and thus ${}^{2}J_{CC} \leq 3$ Hz, which is also close to literature values.

Experimental Section

The spectra of labeled and unlabeled phenylsuccinic acid were taken on a Varian XL-100 nmr instrument at 500 and at 100 sweep widths, using frequency counter calibration of resonances. The concentration of the solutions was 1.0-1.5% (w/v). Spectra at both sweep widths were simulated using the LAOCOON III program adjusted to provide a computer-generated plot of the spectrum.³¹ The parameters were adjusted until the computergenerated plot was superimposable over the observed spectrum. In some cases the iterative operation was used, which led to root mean square errors of 0.08-0.1 between the calculated and observed data sets. Usually the data generated by the iterative procedure required one or two more trial-and-error adjustments before the computer plot and the observed spectrum were identi-The ¹³C spectra were taken on an acetone- d_6 solution (2%) cal. m w/v) using a 1 $m \ddot{K}$ filter, and a 1500-Hz noise band width at m 80%high power operation of the decoupler; 11,000 transients were taken using an acquisition time of 1.3 µsec and a 40-µsec pulse width. Under these conditions, little or no interference of the signal of the labeled carbonyl was observed. The synthesis of the substrate has been reported earlier.³² In this work, signs of coupling constants are not implied unless expressly stated.

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Registry No.-Carbon-13 phenylsuccinic acid, 37729-65-0.

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A New Method for the Preparation of 4-Methylene-1-cyclohexenes

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The direct synthesis of 4-methylene-1-cyclohexenes via the Diels-Alder reaction, using allene as a dienophile and dienes such as 1,3-butadiene, substituted butadienes, and cyclic dienes, is possible only in special cases.^{2,3} 4-Methylene-1-cyclohexenes are usually made by modification of other Diels-Alder adducts. For example, pyrolysis of 3-cyclohexenylmethyl acetate gave a 60% yield of 4-methylene-1-cyclohexene contaminated with toluene.⁴ Treatment of the adduct of cyclopentadiene and methyl α -bromovinyl sulfone with sodium methoxide in dimethyl sulfoxide afforded 5methylene-2-norbornene.⁵ Finally, addition of methyllithium to the Diels-Alder adduct of 1,3-butadiene with 3-chloro-2-(trichlorosilyl)propane gave 4-methylene-1-

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⁽³⁾ Allenes possessing electron-withdrawing groups in conjugation are (4) C. G. Overberger and A. E. Borchert, J. Amer. Chem. Soc., 82, 1007

cyclohexene.⁶ None of these methods is entirely acceptable because of low yields, requirement of harsh conditions, or formation of mixtures of products.

Our experience with α -bromoacrolein $(1)^7$ led us to expect that the Diels-Alder adduct of 1 and various 1,3dienes could be reduced to the bromohydrin 3, which upon treatment with zinc in methanol would give the desired 4-methylene-1-cyclohexenes (4). As expected, α -bromoacrolein reacted smoothly with a variety of 1,3dienes. Adducts were formed from cyclopentadiene in 98% yield, from 2,3-dimethyl-1,3-butadiene in 95% yield, from 1,4-trans,trans-diphenyl-1,3-butadiene in 84% yield, and from anthracene in 69% yield. The order of reactivity of the dienes in the Diels-Alder reaction is as expected: cyclopentadiene > 2,3-dimethylbutadiene > trans,trans-1,4-diphenylbutadiene ~ anthracene.

The adducts 2 could all be easily converted to the bromohydrin 3 in ca. 95% yield by treatment with



excess sodium borohydride in wet tetrahydrofuran at 25° for 2-4 hr. These unusual conditions were found to be very effective in preventing formation of the epoxide or reductive dehalogenation.⁸ Dehalohydrination was best carried out by treatment of **3** with excess activated zinc in methanol to give the isomerically pure 4-meth-ylene-1-cyclohexenes in 80-90% yield.

Experimental Section

Reaction of Cyclopentadiene with α -Bromoacrolein.— α -Bromoacrolein⁹ (1.6 g, 11 mmol) was dissolved in 5 ml of ether at 0°. Cyclopentadiene (0.9 g, 16 mmol) was added and the solution was stirred for 18 hr at 0°. The solvent was evaporated, giving a 7:3 mixture of exo-endo aldehyde 2a in quantitative yield, which was used without further purification: ir (neat) 3030, 2940, 2880, 2700, and 1721 cm⁻¹; nmr (CDCl₃) δ 9.72 (0.7 H, s, exo CHO), 9.48 (0.3 H, s, endo CHO), 6.0-6.8 (2 H, m, CH=), 3.32 1 H, m, CH), 3.00 (1 H, m, CH), 2.1-2.7 (2 H, m, CH₂CBrCHO), and 1.2-2.0 (2 H, m, CH₃).

Reaction of 2,3-Dimethylbutadiene and α -Bromoacrolein.— α -Bromoacrolein⁹ (1.35 g, 10 mmol), potassium carbonate (50 mg), hydroquinone (10 mg), and 2,3-dimethylbutadiene (1 g, 12 mmol) were kept at 55° in 5 ml of benzene under nitrogen for 18 hr. Ether (20 ml) was then added and the solution was filtered and evaporated, giving 2.03 g (95%) of bromo aldehyde 2b: ir (neat) 2985, 2941, 2703, and 1724 cm⁻¹; nmr (CDCl₃) & 9.50 (1 H, s, CHO), 2.62 (2 H, br, CH₂), 2.13 (4 H, br, CH₂), and 1.60 (6 H, br, CH₃).

Reaction of trans, trans-1,4-Diphenylbutadiene with α -Bromo-

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(9) R. H. Baker, S. W. Tinsley, Jr., D. Butler, and B. Rigel, J. Amer. Chem. Soc., 72, 393 (1950). acrolein.—trans,trans-1,4-Diphenylbutadiene (1 g, 5 mmol), α -bromoacrolein⁹ (1.35 g, 10 mmol), potassium carbonate (50 mg), and hydroquinone (10 mg) were stirred in 10 ml of toluene under N₂ for 72 hr at 100°. The solution was cooled, diluted with ether, filtered, and evaporated giving 2.6 g of brown oil. This was purified by preparative tlc (two developments, pentaneether 9:1), giving 1.37 g (84%) of bromo aldehyde 2c. The other compounds present were diphenylbutadiene, α -bromoacrolein, and α -bromoacrolein dimer. The spectral data for 2c are ir (neat) 3030, 2940, 2860, 2700, 1720, 740, and 700 cm⁻¹; nmr (CDCl₈) δ 9.64 (1 H, s, CHO), 7.4 (10 H, br, C₆H₅), 6.0 (2 H, m, CH=), 4.3 (1 H, br, CH), 3.9 (1 H, m, CH), and 1.6-2.8 (2 H, m, CH₂).

Reaction of Anthracene and Bromoacrolein.—Anthracene (0.5 g, 2.8 mmol), α -bromoacrolein⁹ (0.8 g, 6 mmol), potassium carbonate (50 mg), and hydroquinone (5 mg) were stirred in 5 ml of toluene under nitrogen for 4 days at 100°. The solution was cooled, diluted with ether, filtered, and evaporated to give 1.05 g of brown oil which was purified by preparative tlc (pentane-ether 1:1) to give 0.576 g (69%) of 2d and 75 mg of 2-formyl-5-bromo-4*H*-pyran. The Diels-Alder adduct 2d was recrystallized from cyclohexane to give colorless crystals: mp 129-130°; ir (neat) 3030, 2940, 2860, 2700, 1720, and 760 cm⁻¹; nmr (CDCl₃) δ 9.41 (1 H, s, CHO), 7.2 (8 H, m, C₆H₄), 4.67 (1 H, s, CH), 4.3 (1 H, d of d, J = 2.5, 2.5 Hz, CH), 2.94 (1 H, d of d, J = 2.5, 15 Hz, CHH). Reduction of 2a.—The bromo aldehyde mixture 2a (2.3 g,

Reduction of 2a.—The bromo aldehyde mixture **2a** (2.3 g, 11 mmol) was dissolved in 50 ml of THF containing 0.1 ml of water, and sodium borohydride (200 mg) was added. The solution was stirred for 2 hr, and 10 ml of 20% sodium dihydrogen phosphate solution was added to decompose excess borohydride and prevent the halohydrin from forming the epoxide. Water (50 ml) was then added and the solution was extracted with 3 \times 30 ml of ether which was extracted with saturated sodium chloride solution, dried over magnesium sulfate, and evaporated to give 2.1 g (95%) of bromo alcohol mixture **3a**: ir (neat) 3400, 2940, and 1110 cm⁻¹; nmr (CDCl₃) δ 6.0–6.3 (2 H, m, CH=), 3.8 (2 H, m, CH₂), 3.2 (1 H, m, CH), 2.9 (1 H, m, CH), and 1.1–2.1 (4 H, m, CH₂).

Reduction of 2b.—Bromo aldehyde **2b** (1.68 g) was reduced as for **2a**, giving 1.58 g (93%) of bromo alcohol **3b**: ir (neat) 3400, 2940, 1440, 1090, and 1030 cm⁻¹; nmr (CDCl₃) δ 3.7 (2 H, s, CH₂OH), 2.48 (2 H, br s, CH₂), 1.7–2.3 (4 H, m, CH₂), and 1.61 (6 H, s, CH₃).

Reduction of 2c.—Bromo aldehyde 2c (1.0 g) was reduced as previously described for 2a, giving 0.92 g (90%) of bromo alcohol 3c: ir (neat) 3450, 3030, 2970, 1600, 1490, 1450, 760, and 700 cm⁻¹; nmr (CDCl₃) δ 7.3 (10 H, s, C₆H₅), 5.6-6.3 (2 H, m, CH=), 3.6-4.3 (2 H, m, 2 CH), 3.25 (2 H, br s, CH₂O), and 1.5-2.4 (2 H, m, CH₂).

Reduction of 2d.—Bromo aldehyde 2d (0.4 g) was reduced as previously described for 2a, giving 370 mg of bromo alcohol 3d (92%) as colorless crystals. Recrystallization from cyclohexane gave a product melting at 130-132° dec: ir (CHCl₃) 3450, 3030, 2940, and 1470 cm⁻¹; nmr (CDCl₃) δ 7.2 (8 H, m, C₆H₄), 4.81 (1 H, s, CH), 4.32 (1 H, d of d, J = 2.5, 2.5 Hz, CH) 3.55 (1 H, d, J = 12 Hz, CHHO), 3.05 (1 H, d, J = 12 Hz, CHHO), 2.50 (1 H, d of d, J = 2.5, 14 Hz, CHH), and 1.93 (1 H, d of d, J = 2.5, 14 Hz, CHH).

Reaction of Bromo Alcohol 3a with Zinc.—Bromo alcohol **3a** (3.6 g, 18 mmol) was taken up in 100 ml of methanol and stirred for 18 hr at room temperature with 25 g of activated zinc (prepared by stirring zinc dust for 5 min in glacial acetic acid and then washing with several portions of methanol). The reaction mixture was filtered through sintered glass and the residue was washed with 100 ml of pentane and 100 ml of water. After the filtrate and washings were shaken, the pentane layer was removed and the aqueous layer was extracted with 2 × 25 ml of pentane. The combined pentane extracts were dried and the pentane was distilled, giving 1.3 g (65%) of crude 5-methylene-2-norbornene (4a). Evaporative distillation of the residue gave a product which was pure by gc (10 ft 10% TCEP, 50°): ir (neat) 3080, 2940, 2850, 1660, and 880 cm⁻¹; nmr (CDCl₃) δ 6.05 (2 H, m, CH=), 4.92 and 4.70 (2 H, 2 br s, CH₂==), 3.17 (1 H, br, CH), 2.95 (1 H, br, CH), 1.3-2.5 (4 H, m, CH₂). The ir and nmr spectra are identical with those of an authentic sample (Aldrich Chemical Co.).

In a similar experiment using cyclohexane as an internal standard, gpc (10 ft 10% TCEP, 50°) indicated the yield to be 90%.

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Reaction of Bromo Alcohol 3b with Zinc.—The bromohydrin 3b (1.04 g, 4.75 mmol) was dissolved in 30 ml of methanol, and 10 g of activated zinc was added. The solution was stirred overnight and filtered through sintered glass, and the residue was washed with pentane and water. After the filtrate and washings were shaken, the pentane was removed and the aqueous layer was extracted with 2×25 ml of pentane. The combined pentane layers were dried over magnesium sulfate, and the pentane was evaporated at 1 atm, giving 0.52 g (89%) of 1,2-dimethyl-4methylene-1-cyclohexane (4b). Evaporative distillation gave 0.36 g: ir (neat) 3080, 1670, and 885 cm⁻¹; nmr (CDCl₃) δ 4.68 (2 H, br s, =:CH₂), 2.65 (2 H, br, =:CH₂C=:), 2.25 (4 H, m, =:CCH₂), and 1.62 (6 H, s, CH₃).

Anal. Calcd for C₉H₁₄: mol wt, 122.1095. Found: mol wt, 122.1092.

Reaction of Bromo Alcohol 3c with Zinc.—The bromohydrin 3c (0.407 g, 1.14 mmol) in 10 ml of methanol was treated with 1.5 g of activated zinc. After 2 hr the solution was filtered with suction and the filtrate was evaporated to dryness. The residue was taken up in 2% hydrochloric acid which was then extracted with 3×15 ml of pentane, which was dried over magnesium sulfate and evaporated to give 245 mg (86%) of 3,6-diphenyl-4-methylenecyclohexene (4c), pure by tlc and gc: ir (neat) 1650 and 870 cm⁻¹; nmr (CDCl₃) δ 7.36 (10 H, s, C₆H₅), 6.03 (2 H, s, CH=), 4.83 and 4.90 (2 H, 2 s, =CH₂), 4.16 (1 H, br, CH), 3.62 (1 H, m, CH), and 2.42 (2 H, m, CH₂).

Anal. Caled for $C_{19}H_{18}$: mol wt, 246.1408. Found: mol wt, 246.1407.

Reaction of Bromo Alcohol 3d with Zinc.—The bromohydrin 3d (200 mg, 0.53 mmol) was dissolved in 10 ml of methanol, and 1 g of activated zinc was added. After 2 hr the reaction was worked up as described previously for 3c to give 125 mg (83%) of 4d as colorless crystals which were recrystallized from hexane: mp 100-101°;¹⁰ ir (CHCl₈) 1640 and 880 cm⁻¹; nmr (CDCl₈) δ 7.2 (8 H, m, C₆H₄), 5.07 (1 H, br s, CH), 4.68 (2 H, s, =CH₂), 4.27 (1 H, t, J = 3 Hz, CH), and 2.36 (2 H, m, CH₂).

7.2 (3 II, II, C₆II₄), 5.07 (1 II, Dr S, CH), 4.08 (2 II, S, $-CH_2$), 4.27 (1 H, t, J = 3 Hz, CH), and 2.36 (2 H, m, CH₂). *Anal.* Calcd for C₁₇H₁₄: C, 93.54, H, 6.46; mol wt, 218.1095. Found: C, 93.20; H, 6.55; mol wt, 218.1092.

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Registry No.—1, 14925-39-4; exo-2a, 28738-84-3; endo-2a, 28738-83-2; 2b, 41894-54-6; 2c, 41894-55-7; 2d, 41894-56-8; exo-3a, 41915-51-9; endo-3a, 41915-52-0; 3b, 41894-57-9; 3c, 41894-58-0; 3d, 42434-74-2; 4a, 694-91-7; 4b, 41894-60-4; 4c, 41894-61-5; 4d, 19978-14-4; cyclopentadiene, 542-92-7; 2,3-dimethylbutadiene, 513-81-5; trans,trans-1,4-diphenylbutadiene, 538-81-8; anthracene, 120-12-7.

Synthesis and Thermolysis of Thiete 1,1-Dioxide Iron Tetracarbonyl^{1,2}

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> > Received July 3, 1973

Thermolysis of thiete sulfones (thiete 1,1-dioxides) has been suggested to proceed *via* vinylsulfenes as re-

(1) Taken in part from the Ph.D. Thesis of P. L. Chang, Syracuse University, 1970.

(2) Reported at the Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 1971, Abstract 166. active intermediates.³ We have observed that thiete sulfone yields sulfur dioxide at elevated temperatures, indicating the possible formation of three-carbon intermediates such as vinylcarbene, cyclopropene, methylacetylene, or allene. Since a number of reactive intermediates have been obtained as stable complexes of transition metals,⁴ we investigated the synthesis and properties of thiete sulfone iron tetracarbonyl in which the iron atom conceivably could trap vinylsulfene and reactive intermediates formed during the extrusion of sulfur dioxide. Thermolysis of palladium and platinum complexes (1) of thiirene 1,1-dioxides yields an

$$R \xrightarrow{O} R' \xrightarrow{O} RC = CR' + (SO_2)ML_2$$

$$R \xrightarrow{ML_2} R'$$

$$R \xrightarrow{ML_2} R' = Ph_3P$$

acetylene and a complex of sulfur dioxide.⁵ Uncomplexed thiirene 1,1-dioxides also yield an acetylene and sulfur dioxide;⁶ thus thermolysis of 1 is not fundamentally different from the thermolysis of the uncomplexed sulfone.

Pale yellow crystals of thiete sulfone iron tetracarbonyl (3) were obtained (50% yield) either by refluxing a solution of the sulfone 2 in ether with diiron nonacar-



bonyl or by irradiation of 2 and iron pentacarbonyl in benzene.⁷ Under the same conditions no iron complexes could be obtained from 2-sulfolene, 4-phenyl-2H-thiete 1,1-dioxide, or 7-thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide.

The pmr spectrum of **3** shows all protons shifted to higher field relative to the protons of **2**. The chemical shifts of the protons of the double bond show the greatest displacement: $\Delta \delta_{H_a} 1.70$, $\Delta \delta_{H_b} 2.20$, $\Delta \delta_{H_c} 0.93$, $\Delta \delta_{H_d} 0.68$ ppm.⁸ Sulfone absorption in the infrared is essentially unaltered, as is observed in other sulfone complexes,^{8b} and C-H stretching vibrations occur in

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