finding instead utility in asymmetric synthesis as building blocks.[8]

Reaction of the ketene (**3**) derived from racemic ibuprofen (**1**) (Scheme I, Ar = *p*-isobutylphenyl) with chiral α-hydroxy esters gave the 2-arylpropionate esters **4** or **5** in de's of 94–99%.[9] (*S*)-Ethyl lactate provided the *S* stereochemistry and (*R*)-isobutyl lactate the *R* stereochemistry at the benzylic carbon.[10,11] The diastereoselectivity was not affected by the electronics of the aryl ring: phenyl-, 4-methoxyphenyl-, and 4-nitrophenylmethylketenes all showed high selectivity. Substitution of the methyl group with ethyl gave no decrease in selectivity. The naproxen ester [Ar = 2-(6-methoxynaphthyl)] was obtained with a de of 80%.

The reaction of *S*-ethyl lactate with ibuprofen ketene (**3**) was highly dependent on solvent: while more polar solvents lowered the diastereoselectivity, hexanes and heptane were found to be most effective. In cases where the substrate [e.g., naproxen, Ar = 2-(6-methoxynaphthyl)] or the chiral alcohol were insoluble in heptane, toluene was a suitable substitute. Less sterically hindered amines provided higher de's as well as more efficient generation of the ketene. Trimethylamine, dimethylethylamine, and *N*-methylpyrrolidine provided the highest de's (94–99%), while triethylamine (90% de) and diisopropylethylamine (80% de) proved inferior. In the absence of amine the de decreased to 60%. Reaction temperature was not a major factor with only a 7% decrease in de seen in going from −78 °C to room temperature. Optimum conditions with (*S*)-ethyl lactate (**6**) were as follows: −78 °C, 0.02 M; (98.6:1.4 *S,S*/*R,S*); increasing concentration to 1.0 M gave slightly lower selectvity (95:5). The reaction is third order (first order with respect to the ketene, alcohol, and amine) and possesses a pronounced deuterium isotope effect ($k_H/k_D \sim 4$).

A study of the structural effects of the alcohol was carried out to determine the controlling features of the chiral reagent (Table II).[12] This led to the discovery of the completely diastereoselective reagent, (*R*)-pantolactone. Variation of the ester alkyl group did not affect the diastereoselectivity (entries 1–4). However, increased steric bulk adjacent to the hydroxy group had a marked positive effect [cf. (*S*)-ethyl lactate, methyl (*R*)-hexahydromandelate, and (*R*)-pantolactone (entries 1, 5, and 6, respectively)]. The most important feature of the chiral reagent was the proximity of the hydroxyl group to a hydrogen bonding moiety, preferably a carbonyl.[15] If no such group was present, as with an aliphatic alcohol (entry 11), the diastereoselectivity was low. Displacement of the hydroxyl group from the carbonyl by one methylene unit (entry 10) caused a tremendous drop in the diastereoselectivity. The α-hydrogen bonding group can be an ester, amide,[16] or phenyl group as with *sec*-phenethyl alcohol.[5] Alternative sites for hydrogen bonding weaken the key interaction of the α-hydroxyl group and the carbonyl, reducing selectivity (entries 7–9). In all cases the (*S*)- and (*R*)-hydroxy esters provided predominantly the *S* and *R* stereochemistry, respectively. Maximum diastereoselectivity in the ketene addition can be obtaned by the proper grouping of three structural features: a chiral hydroxyl group (1) which is α to a carbonyl group (2) and adjacent to a tertiary alkyl group (3) containing no hydrogen bonding moieties. (*R*)-Pantolactone (entry 6) fits all these criteria and gives remarkable selectivity!

This work provides a practical chiral synthesis of 2-arylaliphatic acids: either enantiomer can be prepared easily with readily available chiral alcohols. The utility of the method is evidenced by the chiral syntheses of ibuprofen and naproxen. The relationship of hydrogen bonding to high diastereoselectivity shown here is far from obvious. Studies toward elucidation of the mechanism of this diastereoselective addition and determination of the scope of α-hydroxy esters as chiral reagents are in progress.

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(9) The generation of the ketene with 300 mol % of amine was followed by infrared spectroscopy. The acid chloride peak of **2** at 1790 cm^{-1} disappeared as the ketene peak of **3** at 2100 cm^{-1} intensified. The chiral reagent was then added neat at −78 °C. The ratio of the diastereomers was easily observed by HPLC: Microsorb C-8 4.6 mm × 150 mm; acetonitrile–water–phosphoric acid 60:40:0.1; 1.5 mL/min; 230 nm.

(10) Optical purity of commercial lactate esters was assayed by HPLC after conversion to the α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) esters (1.1 equiv of triethylamine, 4-(dimethylamino)pyridine, and (*R*)- or (*S*)-MTPA, each, in methylene chloride). Microsorb C-8; acetonitrile–water–trifluoroacetic acid 55:45:0.1, 1.5 mL/min; 230 nm. Cf: (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org Chem.* **1969**, *34*, 2543. (b) Reference 2c.

(11) After the ketene had completely reacted, anhydride (2–5%) generated from extraneous water was selectively cleaved with 3-(dimethylamino)propylamine (ref 10a) or acetic acid–water (4:1; 70 °C). The esters were either hydrolyzed in acetic acid–2 N aqueous hydrochloric acid (5:2, 85 °C) or with LiOH in acetonitrile–water at 5 °C. For a discussion of the saponification of epimerizable acyl derivatives, see: (a) Evans, D. A.; Ellman, J. A.; Dorow, R. L. *Tetrahedron Lett.* **1987**, *28*, 1123. (b) Evans, D. A.; Britton, T. C.; Ellman, J. A. *Tetrahedron Lett.* **1987**, *28*, 6141. Isolated ibuprofen is assayed for chirality by conversion to the benzamides (i. carbonyl diimidazole, isopropyl acetate; ii. benzylamine), and the enantiomers are separated on a chiral Pirkle L-Phenylglycine Covalent column; 97:3 hexanes–isopropy alcohol. For additional discussion on the chiral assay of α-methylarylacetic acids, see: (c) Wainer, I. W.; Doyle, T D. *J. Chromatogr.* **1984**, *284*, 117.

(12) Comparisons were carried out on ketene **3** (derived from ibuprofen) in toluene since many of the chiral alcohols were not soluble in hexanes or heptane at −78 °C.

(13) Benzyl lactate (bp 128 °C, 0.07 mm) was prepared by formation of potassium (*S*)-lactate (potassium hydroxide, 1% aqueous ethanol) and benzylation of the isolated salt (benzyl bromide, DMF, 100 °C).

(14) Methyl (*R*)-hexahydromandelate was prepared by heating a solution of (*R*)-hexahydromandelic acid in methanol-concentrated sulfuric acid (99:1) at reflux.

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(16) (*S*)-Dimethyllactamide (ref 2c) similarly provides high diastereoselectivity. This will be discussed in forthcoming publications.

1,2-Dithiete Is More Stable Than 1,2-Dithioglyoxal As Evidenced by a Combined Experimental and Theoretical IR Spectroscopic Approach

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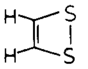
Received December 5, 1988

A photoelectron (PE) spectroscopic study on the pyrolysis of 1,3-dithiol-2-one provided evidence that 1,2-dithiete (**1**) is more stable than its valence isomers *trans*-(**2**)-, *cis*-(**3**)-, or *gauche*-(**4**)-dithioglyoxal.[1] This result was further backed by a microwave



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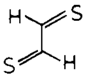

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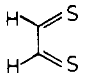

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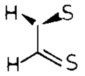

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study[2] on the same reaction and a PE spectroscopic investigation of analogous selenium compounds.[3] Quantum chemical calculations[1,4,5] on the total energies of the various isomers did not yield unambiguous results. However, the most elaborate calculations[5] (optimization of molecular structures on the 6-31G*[6] SCF level, addition of 3-21G*[7] SCF zero-point vibrational, and MP4 SDQ[8] electron correlation energies to the 6-31G* SCF energy minima) determined the trans form to be more stable than the cis and ring forms by ≈4 and ≈7 kcal mol^{-1}, respectively. On the basis of these results, it was suggested[5] that **2** or **4** might also have been present under the experimental conditions at which the PE spectrum was obtained.[1]

We have reinvestigated the pyrolysis of 1,3-dithiol-2-one (at 600, 700, and 800 °C) using the method of low-temperature matrix IR spectroscopy. The spectra were corrected for background absorption (recorded before matrix deposition). Relative (to the 1501-cm^{-1} absorption) integrated absorbances (IR intensities) I_{rel} were derived from the band areas (approximated by height × width). For the identification of the absorption bands of 1,2-dithiete and its isomers the corresponding vibrational frequencies and IR intensities were calculated quantum chemically by taking electron correlation into account.

The spectrum of the reaction mixture at 600 °C essentially reflects undecomposed educt, 1,3-dithiol-2-one, with distinct absorptions at 421, 542, 606, 636, 820, 839, 917, 1652, 1712, and 1754 cm^{-1}. The spectrum of the mixture at 800 °C is dominated by two bands at 1529 and 734 cm^{-1}, which belong to the decomposition products CS_2[9a] and C_2H_2[9b] (additionally characterized by the presence of a band at 3287 cm^{-1}), respectively. A further band at 1276 cm^{-1} being pronounced only in the 800 °C spectrum is presumed to be due to the fragment CS.[9c]

Figure 1a shows the relevant segment of the IR spectrum of the reaction mixture at 700 °C. Many bands, in addition to the ones discussed above, occur in this case. Figure 1b exhibits the relative IR intensities of these bands in a stick diagram. All calculations of the present work were performed on the MP2/6-31G*[8] level of approximation with the program CADPAC.[10] The resulting total energy minima are −872.39260 au for **1**, −872.40131 au for **2**, and −872.39454 au for **4**. A vibrational analysis (MP2/6-31G*) of structure **3** (C_{2v}) gave one imaginary frequency which indicates it to be a transition structure (energy: −872.39438 au). In accordance with the calculations of ref 5 our results indicate that the trans form is predicted to be somewhat more stable than the gauche form and the ring isomer which lie higher in energy by 4.2 and 5.5 kcal mol^{-1}, respectively (the corresponding values with inclusion of zero-point vibrational energies are 4.1 and 5.8 kcal mol^{-1}).[11]

The theoretical spectra for **1**, **2**, and **4** are displayed in Figures 1c–e, respectively, as stick diagrams. Best agreement with experiment was obtained by multiplying (scaling) the calculated harmonic $\tilde{\nu}$ values with a factor of 0.95. The calculated (scaled) frequencies as well as the integrated absorption coefficients of **1** (Figure 1c) are in excellent agreement with the observed bands (Figure 1a) or sticks (Figure 1b) indicated by (●). Thus the following interpretations are suggested (experimental $\tilde{\nu}$ values in cm^{-1} in parentheses): a_1 νSS (494), b_2 δring (566), b_1 γCH (637), b_2 ν_{as}CS (791), a_1 ν_sCS (798), a_1 δ_sSCH (1049), b_2 δ_{as}SCH (1215), and a_1 νCC (1501). Obviously no evident correlation exists between the experimental spectrum and the calculated spectrum of **4**. However, there are two observed bands at 826 and 1223 cm^{-1} (marked (○) in Figure 1 (parts a and b)) which might be ascribed to the two most intense calculated absorptions of **2**. According to a rough estimate based on the theoretical $\mathcal{A}$ values of the strongest absorptions of **1** and **2** ≈10% trans form at maximum (versus 90% ring isomer) would be consistent with the experimental spectrum. Of course, this interpretation is only tentative since the two bands might belong to unidentified compounds like the other unassigned bands. It should be noted that the previously solely available theoretical IR data for **1**–**4**,[5] namely frequencies calculated on the 3-21G SCF level, correlate noticeably worse with

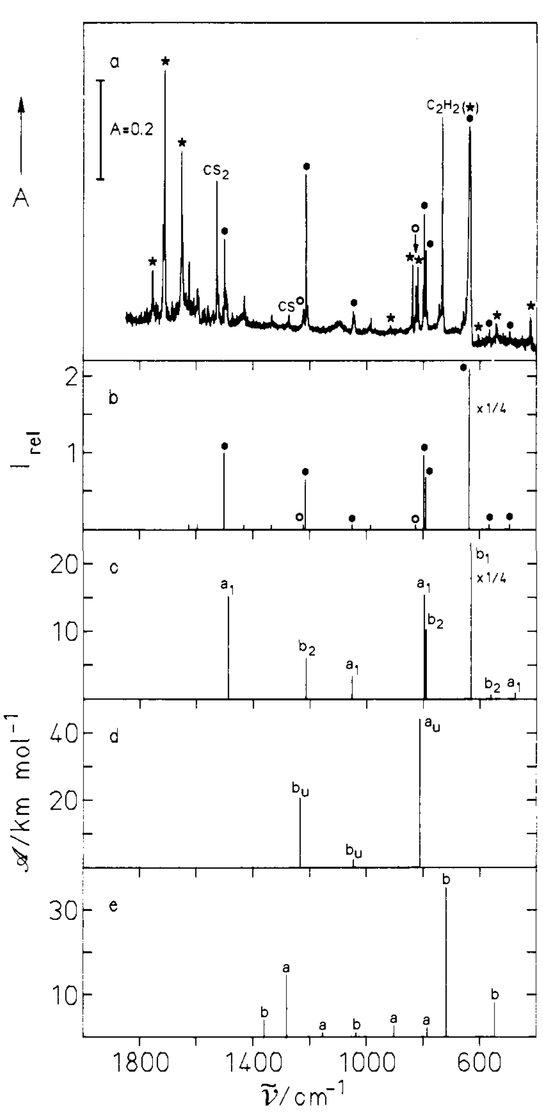

Figure 1. (a) Portion of the IR spectrum (absorbance A vs frequency $\tilde{\nu}$) of the Ar matrix-isolated reaction mixture at 10 K after pyrolysis of 1,3-dithiol-2-one at 700 °C; bands of 1,3-dithiol-2-one, 1,2-dithiete (**1**), and (tentatively) of *trans*-dithioglyoxal (**2**) are indicated by (*), (●), and (○), respectively. (b) Stick diagram (relative intensity I_{rel} vs $\tilde{\nu}$ for the five most intense bands; stick height arbitrary for the other ones) of the additionally occurring (i.e., without the absorptions assigned to 1,3-dithiol-2-one, C_2H_2, CS_2, and CS) bands. (c), (d), and (e) Theoretical (MP2/6-31G*) IR spectra (integrated absorption coefficients $\mathcal{A}$ vs $\tilde{\nu}$; theoretical frequency values scaled with 0.95; symmetry types specified) of 1,2-dithiete (**1**), *trans*-dithioglyoxal (**2**), and *gauche*-dithioglyoxal (**4**), respectively.

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(11) Additional higher level single point calculations on **1** and **2** at their MP2/6-31G* geometries also predicted **2** to be more stable than **1** (energy difference in kcal/mol of **1**–**2** given in parentheses): MP4/6-31G* (7.8), CCD/6-31G* (5.0), and MP2/6-311G* (6.6).

the experimental data (even after scaling the frequencies as proposed[5]).

To summarize the IR data unequivocally suggest 1,2-dithiete to be the most stable isomer, whereas the computed total energies indicate *trans*-dithioglyoxal should be the most stable. The computed energies however do predict that **1** and **2** should be similar in energy. It is not surprising that there is not better quantitative agreement of the computed relative energies with the apparent experimental results, since errors of this magnitude for isomers are not uncommon at this level of calculation.[12]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the National Science Foundation (Instrument Grant CHE 8808018).

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Solid-State NMR Study of Acetylene Adsorbed to Platinum on Alumina As Followed by Direct Observation Using CP MAS Methods. Differentiation between Acetylene Adsorbed to Alumina and Platinum

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In a recent series of papers Slichter and co-workers[1] have reported solid-state ^{13}C and ^{195}Pt NMR investigations of small molecules, e.g., acetylene and ethylene, adsorbed to platinum on η-alumina. Of particular interest to us is the work involving the adsorption of acetylene.[1a] This work is significant because it verified that the principal species on the surface was not the ethylidyne, $\equiv CCH_3$, species proposed by Somorjai et al.[2] Rather, what Slichter and co-workers deduced from their analysis was that the principal component could be described as a species of the type CCH_2 (77 ± 7)% and to a lesser amount (23 ± 7)% HCCH. The C–C bond length of CCH_2 was estimated to be midway between a single and double bond. Slichter and co-workers arrived at their conclusions by a careful analysis of the "slow beats" present in spin-echo amplitudes in the free induction decay and not by direct observation of the high-resolution solid-state ^{13}C spectra via CP MAS methods. Hence, because of the importance of their observations we wanted to confirm them by using more conventional CP MAS methods. Of more concern, however, was the apparent implicit assumption that the acetylene does not react with the alumina support. Such an assumption, if incorrect, would have a striking influence on their structural conclusions. It is apparent from the surface literature that such an assumption is not valid.[3] We confirm that ethylidyne species are not present on Pt/γ-Al_2O_3 surfaces. However, we also prove that acetylene *does* chemisorb to alumina in the presence and absence of platinum metal. Further, the presence of such species adsorbed to the alumina clearly biases the structural conclusions of Slichter and co-workers. Finally, we conclude the principal species bound to the platinum is such that the bonding between the carbon atoms is intermediate between double and triple bonds. This latter conclusion is supported by IR experiments on the Pt/γ-alumina surface.

The samples were prepared by standard methods,[4] and the solid-state ^{13}C data were obtained on a Varian XL-300 by using conventional CP MAS methods.[5] Presented in Figure 1 is the ^{13}C CP MAS NMR spectra of [1,2-^{13}C]acetylene, 90%, adsorbed to γ-alumina and platinum surfaces. Comparison of spectra of adsorbed acetylene on γ-alumina obtained at several spinning speeds and variable temperatures, we can extract four isotropic carbon resonances from spectra a–d in Figure 1. Their chemical shifts are 148, 88, 58, and 23 ppm.[6] These chemical shifts[7] most likely correspond to a mixture of two chemical species on the γ-alumina surface, e.g.

$$\mathrm{Al{-}O{-}CH_2{-}(CH_2)_2{-}CH_3} \qquad (1)$$

$$\mathrm{Al{-}O{-}CH{=}CH_2} \qquad (2)$$

Figure 1e illustrates the ^{13}C CP MAS NMR spectra of [1,2-^{13}C]acetylene, 90%, adsorbed to 5% Pt/γ-Al_2O_3 at room temperature. Additionally, in Figure 1f we present the results of adsorbed acetylene on platinum surfaces where we have subtracted the spectrum in Figure 1d from that of Figure 1e. The criteria employed for the scaling was that the peaks at 148 and 88 ppm would be removed from the difference spectrum. As a result of this procedure four isotropic peaks due to the presence of Pt metal are evident in Figure 1f. Their chemical shifts are 129, 59, 23, and 14 ppm. Clearly, the principal species present on the Pt/γ-alumina surface is represented by the resonance at 129 ppm. The peaks at 59, 23, and 14 ppm may arise from an increase in the population of species[1] in the presence of γ-alumina on platinum surface. This may simply result from the increased loading of acetylene in the presence of the platinum. However, the minor isotropic peaks at 23 and 14 ppm could also possibly arise from the chemical species, Pt–CH_2CH_3.[8] Further, the application of the interrupted ^{1}H-decoupling sequence[9] demonstrates the resonances at 59, 23, and 14 ppm have directly bonded ^{1}H's, and the resonance at 14 ppm can be assigned to a methyl resonance. That is, this resonance is reduced in intensity but not eliminated by the interrupted decoupling sequence.

The results of the interrupted ^{1}H-decoupling experiments show the resonance at 129 ppm has a more complicated behavior. That is, the resonance loses about 50% of its intensity and is narrowed approximately by a factor of two. Hence, we ascribe this resonance to two carbons, one protonated and the other nonprotonated. The

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(4) The sample is cleaned on vacuum line by alternating H_2 and O_2 flow for about 5 h and then evacuated overnight at 298 °C. The ^{13}C-enriched acetylene is loaded, after the sample is cooled down to room temperature in vacuum. In about 40 min, evacuation is performed again to remove any physisorbed C_2H_2. The sample is frozen and stored with liquid N_2 to avoid any possible thermal decomposition during sealing. The sample is packed in a 7-mm zirconia rotor in a vacuum atmospheric drybox with a N_2 atmosphere.

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(6) Chemical shifts are externally referenced to TMS. The resonances in our ^{13}C spectra were referenced to the most shielded resonance in adamantane which has a chemical shift at 29.2 ppm with respect to TMS.

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