Alder dimerization of 2-pyrone appears not to have been observed by the previous workers who have studied its chemistry.

In a previous study[2] it had been noted that the reaction of 2-pyrone with $Me_3SnC{\equiv}CSnMe_3$ (and, by implication, with the silicon and germanium analogs) was an example of a Diels–Alder reaction with "inverse electron demand," in which the greater electron density in the dienophile favors the reaction. On this basis, di-*tert*-butylacetylene would be expected to react with 2-pyrone and the failure of this reaction to occur even under forcing conditions can be ascribed primarily, if not solely, to unfavorable steric factors. Support for this idea was given by the observation that diethylacetylene reacts with 2-pyrone to give 1,2-diethylbenzene in ~12% yield (5 days at 180°). The electron density of the triple bond in di-*tert*-butylacetylene would be expected to be greater than that in the triple bond of diethylacetylene, but the steric hindrance associated with the two *tert*-butyl groups would be substantially greater than that due to two ethyl groups. In the absence of a reactive substrate, 2-pyrone then reacts in part with itself as outlined above.

Experimental Section

Attempted Reaction of 2-Pyrone with Di-*tert*-butylacetylene.—Di-*tert*-butylacetylene,[5] 2.5 g (18 mmol), in 20 g of dry bromobenzene and 1.8 g (19 mmol) of 2-pyrone[6] were placed in a 2.5 × 18 cm heavy-walled Pyrex bomb tube. The contents were cooled to −78° and the tube was evacuated to 0.1 mm and sealed. It then was heated to 200 ± 10° for 24 hr. The contents of the tube were cooled to −78°, the tube was opened, and the reaction mixture was charged into a distillation flask. The low boiling components were removed by trap to trap distillation at 0.05 mm (pot temperature to 95°). The residue was short path distilled *in vacuo* to yield 0.2 g of clear, colorless distillate, bp 65–70° (3 mm). Glc analysis of the distillate indicated that only unreacted starting materials were present. Small crystals were observed in the neck of the distillation apparatus. These, plus the pot residue, were sublimed at 100° (0.05 mm), yielding 0.1 g of an off-white solid whose ir spectrum indicated the presence of 2-pyrone ($\nu_{C=O}$ 1745 cm^{-1}) and an α,β-unsaturated carboxylic acid [major bands at 2710 (m), 2600 (m), 2530 (m), 1690 (s), and 1630 (s) cm^{-1}]. Recrystallization of this solid from water gave a white solid, mp 132–133°, whose ir and nmr spectra were identical with those of an authentic sample of *trans*-cinnamic acid. A mixture melting point with authentic material was undepressed, 132–133°.

Reaction of 2-Pyrone with Diethylacetylene (3-Hexyne).—A similar procedure was used in the sealed tube reaction of 0.994 g (12.1 mmol) of 3-hexyne (Farchan Chemicals) and 1.064 g (11.0 mmol) of 2-pyrone in the presence of 0.1 g of hydroquinone in 3 ml of dry benzene for 5 days at 180 ± 10°. After the lower boiling materials had been removed by trap to trap distillation at 1 mm (pot temperature to 95°), the residue was short path distilled to give 0.17 g (12% yield) of 1,2-diethylbenzene, bp 60° (10 mm), contaminated with minor amounts of starting materials and solvent. Purification by glc (F & M 700, 6-ft 20% Carbowax 20M on Chromosorb P, at 150°) gave material whose glc and spectral properties were identical with those of an authentic sample (Aldrich Chemical Co.).

Registry No.—2-Pyrone, 504-31-4; di-*tert*-butylacetylene, 17530-24-4; diethylacetylene, 928-49-4.

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(5) G. F. Hennion and T. F. Bannigan, *J. Amer. Chem. Soc.*, **68**, 1202 (1946).

(6) H. E. Zimmerman, G. L. Grunwald and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

Sulfonation of Catechin

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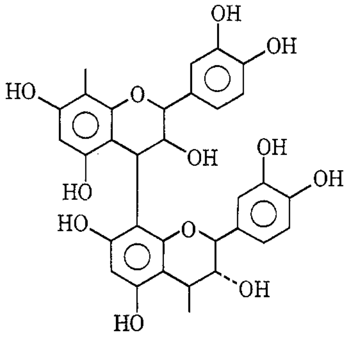
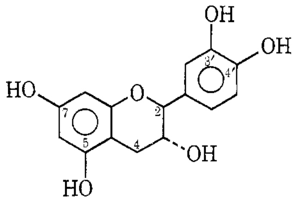
Polyflavanoids of western hemlock bark (*Tsuga heterophylla*) have the structure I, composed of catechin-like units derived from leucocyanidin.[1–3] Extraction of bark with aqueous sodium sulfite–bisulfite yields sulfonated polyflavanoid extracts that have widespread commercial utility.[3] In order to clarify the chemical structure of these materials and to supplement earlier studies,[2,4] a reaction simulating bark extraction conditions was carried out on the flavan catechin (II). No such study has been made on flavans bearing phenolic hydroxyl groups.



I



II

Thin layer chromatographic analysis of material obtained after reaction of catechin with an aqueous solution of sodium sulfite and bisulfite (pH 5.9) for 0.5 hr at 170° showed very little catechin remaining; a spot with low R_f predominated. The acidity of the material and the ease with which it decomposed indicated that sulfonation had occurred. The technique of Gellerstedt and Gierer[5] was used to prepare acetylated methyl sulfonates of the reaction products; a mixture of several components was obtained. Application of an additional acetylation step made one of the products heavily predominant (tlc). Spectral

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(1) H. L. Hergert, Abstracts of Papers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, p 21D.

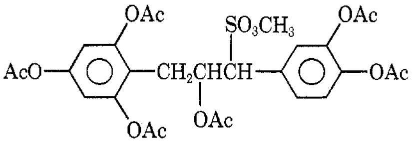
(2) K. D. Sears and R. L. Casebier, *Phytochemistry*, **4**, 359 (1965).

(3) H. L. Hergert, Abstracts of Papers, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, Cell. 66.

(4) K. D. Sears and R. L. Casebier, *Chem. Commun.*, 1437 (1968).

(5) G. Gellerstedt and J. Gierer, *Sv. Papperstidn.*, **15**, 117 (1971).

data for this material, purified by tlc, shows it to have structure III.



III

The nmr spectrum and acetyl analysis shows the presence of six acetyl groups. The two protons in the phloroglucinol ring appear as a singlet, as theory would predict, at τ 3.15. The hydrogen on the carbon bearing the sulfonate group is seen as a one-proton doublet at τ 5.23 with the methyl sulfonate absorption being observed as a singlet at τ 6.20. A small amount of the stereoisomeric epimer which differs in configuration about the carbon bearing the methyl sulfonate group is present; a small singlet (τ 6.35, $-SO_2OCH_3$) and doublet (τ 5.33, $-CHSO_2OCH_3$) for the epimer were observed in the nmr spectrum. The ir spectrum shows strong alkyl sulfonate absorption for III at 1370 and 1180 cm^{-1}. An elemental analysis corroborated the molecular formula as $C_{28}H_{30}O_{15}S$. An attempt to obtain a parent peak by mass spectrum failed; the highest mass observed was at m/e 596, corresponding to $M - 42$ (loss of ketene).

On the basis of these results, it is clear that catechin undergoes ready attack by the sulfonate group at C-2 in the pyran ring. Facile introduction of a sulfonic acid group at this position is reasonable, since it is a benzylic carbon involved in ether formation that is activated to attack by a *p*-hydroxyl group; the corresponding position in lignin molecules was also shown to be readily reactive to acidic sulfonation in recent model compound studies.[5–7] Sulfonation at this position is clearly inhibited by methylation of the *p*-hydroxyl group; reaction of a flavan bearing a 4′-methoxyl group with calcium bisulfite at pH 1.5 and 130° resulted in substitution of a sulfonic acid group at C-2 only after 48 hr.[8]

Experimental Section

Nmr spectra were obtained with a Varian T-60 spectrometer and the ir spectra on a Beckman IR-20 spectrophotometer. Analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Elbach über Engelskirchen, West Germany. Decationizations were carried out with Ionac C-242 resin (H^+ form). Evaporations were *in vacuo* (25 mm).

Reaction of D-Catechin (II) with Aqueous Sodium Sulfite–Bisulfite.—D-Catechin (1.000 g), a mixture of sodium metabisulfite (0.130 g) and sodium sulfite (0.060 g), and water (8 ml) were placed in a small stainless steel vessel that was sealed and heated for 0.5 hr at 170°. After cooling, the solution was diluted with water (75 ml) and decationized.

Processing by the General Method of Gellerstedt and Gierer.[5]—The cation-free solution was adjusted to 50 ml by evaporation and neutralized with aqueous barium hydroxide to pH 8.0. After removal of a small amount of precipitate by centrifuging, the solution was decationized. The solution was neutralized with triethylamine to pH 8.0 and evaporated to dryness. The solids were dissolved in pyridine–acetic anhydride (10 ml of each). After 24 hr, the solution was poured into ice water (150 ml) and stirred for 2 hr. This mixture was evaporated at 40–45°, and the residue was dissolved in water and decationized. The solution was neutralized to pH 8.5 with silver acetate and freeze dried, yield 1.30 g.

The sample was placed in a solution of acetonitrile (125 ml) and methyl iodide (25 ml). The mixture was gently refluxed, with stirring, for 20 hr, during which time more methyl iodide (2 × 10 ml) was added. Solids were removed by centrifuging and the filtrate was evaporated to give 0.90 g. Tlc analysis (silica gel G) using 200:47:15:1 (v/v) benzene:ethanol:water:acetic acid (upper layer) (solvent A) or 5:4:1 (v/v) toluene:ethyl acetate:formic acid (solvent B) with I_2 visualization showed a mixture of four to five components.

Preparation and Isolation of 1-Methylsulfonate-(3,4-diacetoxyphenyl)-2-acetoxy-3-(1,3,5-triacetoxyphenyl)propane (III).—The product (0.90 g) of the preceding sequence was placed in benzene (200 ml). Sodium acetate (1.5 g) and acetic anhydride (2 ml) were added. The suspension was refluxed overnight with stirring; the condenser was fitted with a drying tube. After cooling, the mixture was poured into water (v/v) and stirred for 0.5 hr. The benzene layer was removed using a separatory funnel. Two additional extractions were carried but with benzene. Drying ($MgSO_4$) and evaporation gave 0.254 g of III. Tlc showed only one major spot upon development with solvents A and B and I_2 visualization. Purification by preparative tlc using solvents A and B gave purified III as an amorphous, white solid. The material was stored under N_2 to prevent decomposition: nmr ($CDCl_3$) τ 2.72 (m, 3), 3.15 (s, 2), 4.42 (m, 1), 5.23 (d, 1, $J = 7$ Hz), 6.20 (s, 3), 7.12 (m, 2), 7.73 (m, 15), 8.08 (m, 3) (nmr spectra were also obtained in CD_3CN and CD_3COCD_3); ir ($CHCl_3$) 1770 (s), 1370 (s), and 1189 cm^{-1} (s). An attempt to crystallize purified III (CH_2Cl_2 and C_6H_{14}) gave an amorphous white solid that melted at 68°. *Anal.* Calcd for $C_{28}H_{30}O_{15}S$: C, 52.66; H, 4.74; S, 5.02. Found: C, 52.55; H, 4.87; S, 4.89. Calculated acetyl analysis for six acetyl groups: 40.4%. Found: 37.7%.

Registry No.—II, 154-23-4; III, 35639-04-4.

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α,β-Ethylenic Sulfones from Sulfonomethylphosphonate Carbanions and Aldehydes and Ketones

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For our current investigation into the reactions of organocopper reagents with α,β-unsaturated sulfur compounds, we required an efficient method for converting aldehydes and ketones to vinylic sulfones. α,β-Ethylenic sulfones have been prepared in various ways.[2] Oxidation of ethylenic sulfides to sulfones can be accomplished with hydrogen peroxide in acetic acid, but the yields of unsaturated sulfone are generally low.[3] The most direct procedure is reaction of a carbonyl substrate with the anion of a sulfonomethylphosphonate ester (**1a**, **1b**). This Horner–Wittig reaction using sodium hydride or sodium methoxide at room temperature to generate the phosphonate anion

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[1] NSF Trainee, 1970–present.

[2] I. C. Popoff, J. L. Dever, and G. R. Leader, *J. Org. Chem.*, **34**, 1128 (1969), and references cited therein.

[3] (a) V. Baliah and S. Shanmuganathan, *J. Indian Chem. Soc.*, **35**, 31 (1958). (b) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961). (c) In our hands, hydrogen peroxide–acetic acid oxidation of methyl cyclohexylidenemethyl sulfide (prepared from cyclohexanone) and *trans*-methyl styryl sulfide (prepared from benzaldehyde) to the corresponding vinylic sulfones proceeded in 33 and 40% overall yields (from cyclohexanone and benzaldehyde, respectively).