Distillation of the residue afforded 12.5 g of recovered limonene and 5.89 g (57% based on limonene consumed) of **3** as a colorless oil, bp 72–84° (0.1–0.15 mm) [lit.[6] bp 80–83° (0.2–0.3 mm)], glpc purity 94% (column B, 225°); the ir and nmr spectra were identical with the published spectra of **3**.[6]

3-*p*-Tolyl-1-butanol (4).—To 30 ml of vigorously stirred, anhydrous ethylenediamine at 100–110° was added 0.417 g (0.06 g-atom) of lithium wire in small pieces over a period of 30 min. When the blue color of the solution had disappeared, the mixture was heated to reflux, and a solution of 1.0 g (0.006 mol) of **3** in 5 ml of ethylenediamine was added. The solution was refluxed for 45 min, and then was cooled in ice while 70 ml of water was added. The resulting mixture was extracted with three portions of ether, and the combined extracts were washed with 5% sodium chloride solution, dried, and evaporated to afford 0.90 g of oil. Molecular distillation [bath temperature >60° (0.1 mm)] of this material afforded 0.71 g (72%) of **4** as a colorless oil: glpc purity 94% (column A, 200°); the ir spectrum was in close agreement with published ir data for **4**;[12] nmr (CDCl$_3$) τ 3.02 (s, 4 H, *p*-CH$_3$C$_6$H$_4$–), 6.60 (t, 2 H, J = 7 Hz, –CH$_2$OH), 7.12 (s, 1 H, –OH), 7.25 (m, 1 H, C$_7$H$_7$CHCH$_3$–), 7.78 (s, 3 H, *p*-CH$_3$C$_6$H$_4$–), 8.27 (q, 2 H, J = 7 Hz, –CH$_2$CH$_2$OH), and 8.81 (d, 3 H, J = 7 Hz, C$_7$H$_7$CHCH$_3$–).

1-Bromo-3-*p*-tolylbutane (5).—To 0.38 ml (4.0 mmol) of freshly distilled phosphorus tribromide cooled to 0° was added a solution of 0.66 g (4.0 mmol) of **5** in 2 ml of anhydrous petroleum ether. The mixture was stirred at room temperature for 18 hr, and then was poured into 10 ml of cold water. The resulting mixture was extracted with four portions of ether, and the combined extracts were washed twice with water and then dried and evaporated to afford 0.80 g of oil. Molecular distillation [bath temperature >80° (0.07 mm)] of this material afforded 0.38 g (42%) of **5** as a pale yellow oil: glpc purity 92% (column A, 200°); the ir spectrum was in close agreement with published ir data for **5**;[3] nmr (CDCl$_3$) τ 3.00 (s, 4 H, *p*-CH$_3$C$_6$H$_4$–), 6.86 (m, 2 H, –CH$_2$Br), 7.16 (m, 1 H, C$_7$H$_7$CHCH$_3$–), 7.77 (s, 3 H, *p*-CH$_3$C$_6$H$_4$–), 8.00 (m, 2 H, –CH$_2$CH$_2$Br), and 8.80 (d, 3 H, J = 7 Hz, C$_7$H$_7$CH-CH$_3$–).

(±)-*ar*-Artemisene (2-Methyl-6-methylene-10-*p*-tolyl-2-undecene) (8).—To a stirred solution of 5.0 ml (7.5 mmol) of 1.5 M *n*-butyllithium in hexane was added 0.87 g (7.5 mmol) of dry TMEDA followed by 1.86 g (15.0 mmol) of geraniolene (**6**). The resulting mixture was stirred for 3 hr at room temperature, after which a 2.3-ml aliquot was removed, placed in a separate flask, and cooled below 0°. To this aliquot was added dropwise 0.354 g (1.56 mmol) of **5**. The reaction mixture was allowed to warm to room temperature over a period of 45 min, diluted with water, and extracted with three portions of ether. The combined extracts were washed successively with 5% sodium chloride, 1 M hydrochloric acid, 5% sodium chloride, 2% sodium bicarbonate, and 5% sodium chloride solutions, and were dried and evaporated. Molecular distillation of the residue afforded 0.245 g (58%) of colorless oil. Glpc analysis of this material (column C, 240°) showed a mixture in which the component with longest retention time (65 min) was a single major constituent representing *ca.* 50% of the total. This substance was purified by preparative glpc (column C, 240°) followed by molecular distillation to afford (±)-*ar*-artemisene as a colorless oil: bp (bath) 110° (0.03 mm) [lit.[2b] bp 110° (4–5 mm)]; glpc purity 100% (column B, 240°); ir (film) 3075 (>C=CH$_2$), 3050 and 3020 (–C$_6$H$_4$–), 3010 (>C=CH–), 1649 (>C=CH$_2$), 1519 (–C$_6$H$_4$–), 1456, 1380, 1311 (w), 1110, 1044 (w), 1026, 990 (w), 894 (>C=CH$_2$), 822 (*p*-C$_6$H$_4$–), and 730 cm^{-1} (this spectrum agrees closely with published ir data for **8**[1,2]); nmr (CDCl$_3$) τ 3.00 (s, 4 H, *p*-CH$_3$C$_6$H$_4$–), 4.94 [m, 1 H, –CH=C(CH$_3$)$_2$], 5.36 (broadened s, 2 H, >C=CH$_2$), 7.39 (m, 1 H, C$_7$H$_7$CHCH$_3$–), 7.75 (s, 3 H, *p*-CH$_3$C$_6$H$_4$–), 7.9–8.2 (m, 6 H, allylic –CH$_2$–), 8.3–8.8 [m, 10 H, including 8.34 and 8.43 (two broadened s, –CH=C(CH$_3$)$_2$)], and 8.80 (d, 3 H, J = 7 Hz, C$_7$H$_7$CHCH$_3$–); mass spectrum (70 eV) m/e (rel intensity) 270 (7), 255 (1), 227 (13), 201 (1), 199 (2), 185 (6), 171 (4), 159 (12), 157 (7), 145 (26), 132 (65), 131 (21), 119 (100), 109 (35), 105 (25), 91 (19), 69 (74), 55 (12).

Anal. Calcd for C$_{20}$H$_{30}$: C, 88.82; H, 11.18. Found: C, 89.01; H, 11.20.

Registry No.—**8**, 19907-39-2.

Acknowledgment.—The technical assistance of Mr. F. W. Vonderahe is gratefully acknowledged.

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The Diels–Alder Dimerization of 2-Pyrone

DAVID L. WHITE AND DIETMAR SEYFERTH*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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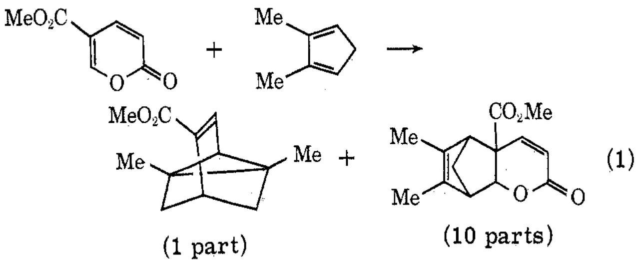
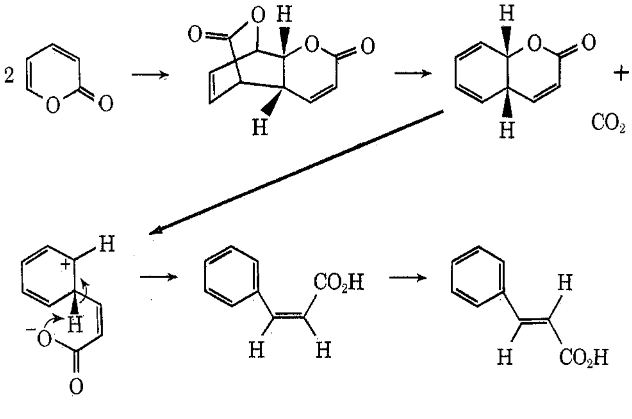
The recent report by Imagawa, *et al.*,[1] concerning reactions in which a 2-pyrone (methyl coumalate) functions as a dienophile (rather than as a diene) in a Diels–Alder reaction (eq 1) prompts us to relate an observation made during the course of our studies of the Diels–Alder reactions between 2-pyrone and group IVB element substituted acetylenes.[2,3] Although the reaction of 2-pyrone proceeded well with acetylenes such as Me$_3$SiC≡CSiMe$_3$,[3] Me$_3$GeC≡CGeMe$_3$,[3] and Me$_3$SnC≡CSnMe$_3$,[2] the expected adduct, 1,2-di-*tert*-butylbenzene, could not be obtained on attempted reaction with di-*tert*-butylacetylene, even after solutions of the reactants in bromobenzene had been heated in a sealed tube at 210° for 5 days. However, a white solid, subsequently identified as *trans*-cinnamic acid by mixture melting point and comparison of its ir and nmr spectra with those of an authentic sample, was isolated from such a reaction mixture in low yield. The formation of this unexpected product was explained[4] in terms of a Diels–Alder reaction of 2-pyrone with itself, the dienophilic C=C bond being the 5,6 double bond as in the examples of the Japanese workers (Scheme I).



SCHEME I



The strenuous reaction conditions would serve to explain the degradative process outlined. Such Diels–

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(1) T. Imagawa, N. Sueda and M. Kawanisi, *J. Chem. Soc., Chem. Comm.*, 388 (1972).

(2) A. B. Evnin and D. Seyferth, *J. Amer. Chem. Soc.*, **89**, 952 (1967).

(3) D. Seyferth and D. L. White, *J. Organometal. Chem.*, **34**, 119 (1972).

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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.

Acknowledgments.—The authors are grateful to the National Science Foundation (Grant GP 31429X) for generous support of this work and to the IBM Corp. for the award of a fellowship to D. L. W.

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Sulfonation of Catechin

Karl D. Sears

Olympic Research Division, ITT Rayonier, Inc.,
Shelton, Washington 98584

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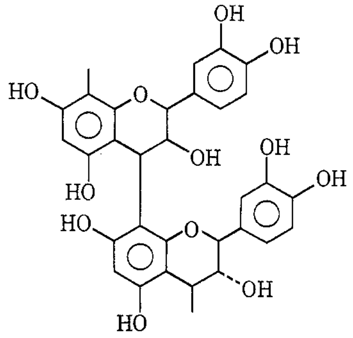
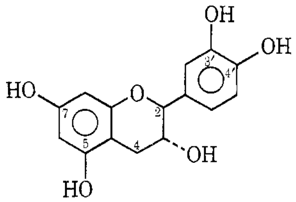
Polyflavanoids of western hemlock bark (*Tsuga heterophylla*) have the structure I, composed of catechin-like units derived from leucocyanidin.[1–3] Extraction of bark with aqueous sodium sulfite–bisulfite yields sulfonated polyflavanoid extracts that have widespread commercial utility.[3] In order to 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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