glucose, fructose, some unknown glucosides and phenolic materials, and trace amounts of several oligosaccharides.

Hot Water Extraction of Quaking Aspen Leaves.—Leaves were freshly obtained from a quaking aspen (*P. tremuloides*) 11 years old felled in Appleton, Wisconsin, on July 25, 1960. A sample of 870 g. (oven-dry basis) was extracted with boiling water and processed in the same manner to yield 5.1 g. of populin identical in all respects with that obtained from the bigtooth aspen leaves. The yield amounted to 0.58% on the basis of the original leaf solids.

The ethyl acetate extract yielded all the spots on paper chromatograms noted for the analogous bigtooth aspen leaf extract plus two purple spots with the diazo reagent at R_f's 0.57 and 0.72.

Populin from September and October Leaves of Bigtooth Aspen.—Green leaves from a *P. grandidentata* felled on September 22, 1960, and yellow leaves from a *P. grandidentata* collected on October 10, 1960, were processed in the manner described. These two bigtooth aspens were from the same clone as the July 21 tree. The September 22 leaves yielded 0.83% populin and the October 10 leaves yielded 0.54% populin based on the original oven-dry leaves. Further processing of both aqueous extracts gave results entirely similar to those obtained with the earlier leaves of bigtooth aspen.

Evaluation of Insoluble Lead Salts.—The precipitated lead salts from the original bigtooth aspen leaf extract were covered with 4 l. of water and treated with hydrogen sulfide with vigorous mechanical stirring. With continued hydrogen sulfide introduction, the mixture was heated to boiling and then boiled without hydrogen sulfide introduction. The hot mixture was filtered, and the cooled filtrate was extracted with ether to yield 0.25% of ether extractives based on original leaf solids. The ether extractives were chromatographed qualitatively on paper in 10:3:3 butanol–pyridine–water, butanol saturated with 2% aqueous ammonia, 0.3 *N* sulfurous acid, and benzene saturated with formic acid developers, and the chromatograms were examined by means of fluorescence under ultraviolet light and 2,4-dinitrophenylhydrazine and diazotized *p*-nitroaniline spray reagents as outlined earlier.[12] These qualitative chromatograms indicated the presence of substantial amounts of vanillic acid, syringic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, ferulic acid, vanillin, syringaldehyde, and acetovanillone. In addition, several unidentified phenolic compounds were indicated.

Similar processing of the lead salts from the original quaking aspen leaf extract yielded essentially the same results except that syringic acid and syringaldehyde were absent.

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Palladium-Catalyzed Decarbonylation of *trans*-α-Substituted Cinnamaldehydes

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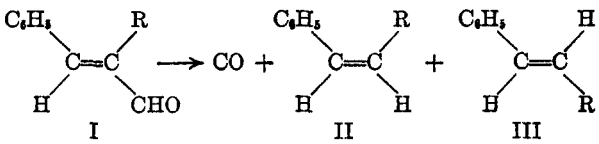
Palladium has been used as a catalyst for liquid phase decarbonylation of aldehydes[1,2] and olefin double bond isomerization.[3] The purpose of the work presented herein was to determine the stereoselectivity of decarbonylation of α,β-unsaturated aldehydes. The investigation appeared worth while in view of the proximity of the olefinic portion of the aldehyde to the reaction center during decarbonylation and, therefore, the possibility of simultaneous configurational olefinic isomerization at the active palladium site.

trans-Cinnamaldehydes (I) were decarbonylated and the product examined for the normal *cis* olefin (II) and the isomerized *trans* olefin (III). Decar-



I II III

R = CH_3, C_2H_5, *i*-C_3H_7, *n*-C_3H_7, C_6H_5

bonylation was performed in two ways. In method A the product was distilled as rapidly as possible after formation, and in method B the reaction mixture was distilled to remove product only after decarbonylation was complete. Results are shown in Table I.

The results show that in the majority of cases decarbonylation by method A gave mainly the normal *cis* product. If it were possible to remove the product *immediately* after formation the ratio of *cis* to *trans* isomer would be higher, and possibly the *cis* isomer would be the sole product. When the initial reaction product was allowed to remain in contact with the catalyst until decarbonylation was complete, method B, III became the main olefin product. Infrared examination of the unchanged aldehyde showed no isomerization in the reactant. Formation of the *trans* olefin, therefore, resulted from isomerization of II.

That the particular catalyst used in this work was capable of isomerizing olefins in the absence of aldehydes is shown in Table II where the results of isomerization of allylbenzene and *cis*-β-methylstyrene are presented. *cis-trans* Isomerization was rapid compared to decarbonylation, and double bond migration was roughly comparable in rate to decarbonylation.

On prolonged contact with the catalyst a saturated-side-chain product also appeared in decarbonylation except in the case of α-methyl- and α-phenylcinnamaldehyde. The reduction was slow compared to decarbonylation especially at lower temperatures. Thus α-methylcinnamaldehyde was completely decarbonylated before a detectable amount of *n*-propylbenzene was formed. However, failure of α-phenylcinnamaldehyde to undergo this reaction cannot be attributed to the same cause and must be related to the structural requirements of the reaction.

(1) H. E. Eschinazi, *Bull. soc. chim. France*, 967 (1952).
(2) J. O. Hawthorne and M. H. Wilt, *J. Org. Chem.*, **25**, 2215 (1960).
(3) G. Egloff, G. Hulla, and V. I. Komarewsky, "Isomerisation of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942, pp. 264, 366.

TABLE I

DISTRIBUTION OF PRODUCTS FROM *trans* α-SUBSTITUTED CINNAMALDEHYDES

Cinnamaldehyde	Method	Temp.,[a] °C.	Time,[b] Hr.	% Styrene *cis*	% Styrene *trans*	% Alkyl benzene	% Yield[c]
CH_3	A	180	23	85	16	0	92
CH_3	B	180	24	10	90	0	48
C_2H_5	A	210	23	61	34	4	85
C_2H_5	B	200	46	10	21	67	49
n-C_3H_7	A	200	18	35	41	22	48
n-C_3H_7	B	210	74	8	12	77	49
i-C_3H_7[d]	A	205	[e]	35	48	5	48
i-C_3H_7[d]	B	210	45	3	13	62	48
C_6H_5	A	200	4	78	22	0	[f]
C_6H_5	B	190	69	64	35	0	42

[a] Initial temperature. [b] Reactions were run overnight. The times listed show the interval from the start of reaction to the following morning or one or two mornings later, when the reaction was found completed. [c] Based on a distillation fraction of wide enough boiling range to include olefin isomers and saturated side chain product. [d] Two compounds other than those listed were formed, presumably olefin isomers. However, the infrared spectra of the compounds did not appear to have bands expected for the isopropenyl or isopropylidene group. [e] Not recorded. [f] Reaction run only to 15% completion.

TABLE II

ISOMERIZATION OF C_3-ALKENYLBENZENES

Reflux temp.; 1 wt. % catalyst

Reactant	Time, hr.	% Allylbenzene	% β-Methylstyrene *cis*	% β-Methylstyrene *trans*
Allylbenzene	1	84	4	12
Allylbenzene	3	72	5	23
Allylbenzene	8	51	9	43
cis-β-Methylstyrene	0.5	1	82	15
cis-β-Methylstyrene	2.5	1	51	48

Pure alkenylbenzenes also gave this reaction, and, therefore, the alkylbenzenes arose after decarbonylation, and the reaction is neither an aldehyde reaction nor is it necessarily promoted by an aldehyde.

$$C_6H_5CH{=}CHR + 2H \longrightarrow C_6H_5CH_2CH_2R$$

The hydrogen source in this reaction must be the alkenylbenzene. A product of approximately twice the molecular weight of the alkenylbenzene was formed in the disproportionation. The structure of this product and the nature of the reaction are currently being studied.

The formation of alkylbenzenes during decarbonylation is not the first example of an unexpected result in decarbonylation. Hawthorne and Wilt have observed extensive dehydrogenation accompanying the decarbonylation of heptaldehyde.[4] These results along with the observed *cis-trans* isomerizations point up the caution that should be exercised in using palladium-catalyzed decarbonylation in structure proof and synthetic work.

Because of the ease of preparation of the *trans*-cinnamaldehydes and the stereoselectivity of the decarbonylation, a combination of these two methods appears to be a simple way of preparing *cis*-β-methyl- and *cis*-β-ethylstyrene.[4] Although yields in the decarbonylation of the other cinnamaldehydes were not very high, the ratio of *cis* to *trans* olefin product was greater than the equilibrium ratio. For this reason decarbonylation could be useful in preparing these *cis* isomers also.

(4) The *cis*-methyl isomer is separable from *cis* rich *cis-trans* mixtures by efficient distillation. See R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953). We were able to get some separation of ethyl isomers, as noted by changes in the infrared spectra of the fractions, with only a crude distillation from an 8-in. Vigreux column.

Experimental[5]

Aldehyde Preparation and Configuration.—α-Substituted cinnamaldehydes were prepared by the base-catalyzed condensation of benzaldehyde with the proper α-unsubstituted aldehyde according to the method of Kraft.[6] These methods were used to establish configurational homogeneity of the cinnamaldehydes: (1) semicarbazones of the aldehydes, prepared in yields of 55–65%, were repeatedly recrystallized and their infrared spectra examined for changes; (2) cinnamic acids, prepared by silver oxide oxidation of the aldehydes, in yields of 80–90%, were repeatedly recrystallized and their infrared spectra examined for changes; and (3) the aldehydes were gas chromatographed on 20% Silicone Dow 11 on firebrick to separate geometric isomers. All methods showed the aldehydes were homogeneous.

The configuration of the aldehydes except α-isopropylcinnamaldehyde was established as *trans* through oxidation to known *trans*-cinnamic acids.[7-9] α-Isopropylcinnamaldehyde resisted silver oxide oxidation. It was assumed to be *trans* by analogy between the product distribution in its decarbonylation and that of the other cinnamaldehydes. Table III lists melting points of the cinnamaldehyde derivatives.

The semicarbazone of *trans*-α-*n*-propylcinnamaldehyde is a new compound.

Anal. Calcd. for $C_{13}H_{17}N_3O$: C, 67.53; H, 7.41; N, 18.18. Found: C, 67.37; H, 7.30; N, 18.30.

Decarbonylation.—Aldehydes, 40 to 100 g., were mixed with 1 wt. % of a 10% palladium in charcoal catalyst. The catalyst was prepared according to the method of Mozingo[10] with Norit SG Extra charcoal.[11] Reaction was conducted

(5) Microanalyses were performed by Schwarzkopf Microanalytical Laboratory. Melting points are uncorrected.

(6) W. M. Kraft, *J. Am. Chem. Soc.*, **70**, 3569 (1948).

(7) R. Stoermer, *Ann.*, **409**, 13 (1915).

(8) R. Stoermer and G. Voht, *ibid.*, **409**, 36 (1915).

(9) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **54**, 334 (1932).

(10) R. Mozingo, *Org. Syn.*, **26**, 77 (1946).

(11) The charcoal was a gift from the American Norit Co.

TABLE III

MELTING POINTS OF α-SUBSTITUTED CINNAMALDEHYDE DERIVATIVES

Cinnamaldehyde	Semicarbazone		trans-Cinnamic acid	
	Found, °C.	Lit., °C.	Found, °C.	Lit., °C.
Methyl	209–210	207–208[a]	79–80.5[b]	81–82[c]
Ethyl	212–214	216–217[d]	103.5–105.5	104[c]
n-Propyl	179.5–181[e]	...	93–94[e]	93[f]
i-Propyl	193–195	191–192[g]		
Phenyl	199–201	194–195[h]	173–173.5	172[i]

[a] K. von Auwers, *Ber.*, **45**, 2764 (1912). [b] Mixed m.p. 79–81.5. [c] Ref. 8. [d] Y. Deux, *Compt. rend.*, **208**, 1090 (1939). [e] Neut. equiv. calcd.: 190.2; found, 191.5. [f] Ref. 9. [g] P. Shoruigin, V. Isagulyantz, E. Smolyaninova, K. Bogacheva, and S. Skoblinskaya, *J. Russ. Phys. Chem. Soc.*, **62**, 2033 (1930); *Chem. Abstr.*, **25**, 4247 (1931). [h] H. Burton, *J. Chem. Soc.*, 748 (1932). [i] Ref. 7.

in a Vigreux distillation apparatus under a vacuum chosen to give reflux at the desired initial temperature. When reaction was allowed to go to completion before distillation, completion was detected by a leveling off of temperature below the initial temperature. Products were redistilled through an 8-in. or 14-in. Vigreux column.

Analysis.—The components of the reaction product were separated and isolated by the use of a 5 ft. 1/2 in. 20% Ucon polar on firebrick gas chromatographic preparative column operated about 50° below the boiling point of the lowest boiling component in the mixture. The reaction products were then analyzed quantitatively by use of a 5 ft. 1/4 in. Ucon polar on firebrick column. The sample volume–area constants of the components for this column were determined by injecting the pure components previously separated by the preparative column. For qualitative analysis the infrared spectra of the components separated by the preparative column were used. Characteristic olefin bands in the infrared spectra[12,13] of the pure olefin products were used to identify their geometric configuration. Alkylbenzenes were identified by comparison of their spectra to cataloged infrared spectra[14] or spectra of samples prepared by a combination of Friedel-Crafts acylation and Clemmensen reduction.

Isomerization of Alkenyl Benzenes.—Isomerizations were run under nitrogen with 5 cc. alkenyl benzene samples having 0.050 g. of the catalyst mentioned above. Time errors were minimized by inserting the samples in an oil bath maintained at 180–200° and quenching the reaction mixture in an ice bath after the proper time interval. The samples were then analyzed by gas chromatography employing the 1/4 in. Ucon polar column previously mentioned.

Disproportionation of Alkenyl Benzenes.—When allylbenzene, α-methylstyrene and β-ethylstyrene were refluxed under nitrogen with 10 wt. % catalyst, amounts detectable by gas chromatography of *n*-propyl-, isopropyl-, and *n*-butylbenzene respectively were formed. A fraction, b.p. 160–161° (3 mm.) was isolated from the β-ethylstyrene disproportionation.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.54; H, 8.45. Found: C, 91.90; H, 8.43.

Mol. wt. calcd. for $C_{20}H_{22}$: 262. Found by benzene boiling point elevation in a McCoy apparatus capable of an accuracy within 5 to 10%: 270.

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

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(14) "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology.

Reactions of 2*H*,3*H*-Thieno[3,2-*b*]pyrrol-3-one. V.[1,2] The Reaction of 2,3-Disubstituted Thieno[3,2-*b*]pyrroles with Oxalyl Chloride

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The recent synthesis of 2-carbethoxy-3-hydroxythieno[3,2-*b*]pyrrole (II)[3] by carbethoxylation of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (I)[4] has made available a product which might be expected to be of value in the preparation of 6-substituted thieno[3,2-*b*]pyrrole derivatives. It was shown[3] that the dimeric enol ester II can be converted readily to the corresponding 3-tosyloxy (III) and 3-acetoxy (IV) derivatives; appropriate substitution reactions on these two products, followed by detosylation or deacetylation, decarbethoxylation, and aromatization of the sulfur-containing ring by methods employed earlier,[3,4] should therefore provide routes to 5- or 6-substituted thieno[3,2-*b*]pyrroles which are not readily accessible by direct substitution reactions.[5–8]

In studies still in progress,[8] III has been converted to the 6-formyl and 6-dimethylamino derivatives under the reaction conditions commonly employed in the preparation of analogous 3-substituted indoles. The present report concerns a study of the reactivity of III and IV towards oxalyl chloride, which in the past has found wide application in the synthesis of tryptamine analogs *via* the corresponding 3-acylindoles.[9–24]

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