Butoxide Method for Phenylchlorocarbene (I, III, IV, VII, VIII, IX, X).—An 80-mmole sample of potassium *t*-butoxide was prepared in a 50-cc. three-neck flask, fitted with condenser and dropping funnel. The excess *t*-butyl alcohol was removed under reduced pressure, 120 mmoles of the indicated olefin was added, and heat was supplied until the olefin began to reflux. A 40-mmole sample of benzal chloride was added dropwise (*p*-methylbenzal chloride was added as a solution in 10 ml. of olefin) over a period of 30 min. The reaction mixture was maintained at reflux and stirred magnetically for at least 3 hr. In cases where the olefin boiled below 70°, the refluxing time was extended to upward of 5 hr. The product was washed three times with water, once with dilute hydrochloric acid, again with water, and dried over sodium sulfate. Olefin was removed under reduced pressure and the adduct vacuum distilled over a short Vigreux column. Redistillation afforded analytical samples.

Methyllithium Method for Phenylchlorocarbene (II, V, VI, X.)—A 100-mmole sample of benzal chloride and 1 mole of the indicated olefin (except adduct II where 40 mmoles of halide and 120 mmoles of olefin were used) were put in a dried nitrogen-filled, three-neck, 250-ml. flask, fitted with a Dry Ice condenser and an addition tube connected to a storage-buret containing methyl lithium (1–2 *N* in ether). The base was added dropwise until an excess of 20% was obtained; the reaction mixture was maintained at 0° by an ice bath and was magnetically stirred. After addition was completed, excess olefin was allowed to evaporate, and the mixture was then washed three times with water and dried over sodium sulfate. Ether was removed under reduced pressure and several vacuum distillations afforded the product.[9]

Acknowledgment.—The author wishes to acknowledge the invaluable counsel of Dr. Gerhard Closs and the financial stability lent by a National Science Foundation Cooperative Fellowship.

(9) Some styrene or *p*-methylstyrene is always formed in this reaction because of the reaction of methyllithium with the arylchlorocarbene. Styrene formation may be minimized by slow addition of the methyllithium.

1,2,3,4-Tetrachloronaphthalene from Trichloroethylene and Benzoyl Peroxide

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Received February 5, 1962

During a study of the action of benzoyl peroxide on trichloroethylene, a colorless crystalline compound (I) of empirical formula $C_5H_2Cl_2$ was isolated after the separation of the major products pentachlorobutadiene and hexachlorobutene.[1] Doubling this formula gives the molecular formula of tetrachloronaphthalene, and a survey of the literature revealed three known tetrachloronaphthalenes with melting points near that of I. The infrared spectrum of I corresponded exactly with that given in the literature for 1,2,3,4-tetrachloronaphthalene[2] and was markedly different from those of the other two. The melting point of I was also closest to those reported for the 1,2,3,4-isomer.

A possible mechanism for the formation of 1,2,3,4-tetrachloronaphthalene is the initiation of a polymer chain of two units of trichloroethylene by a phenyl radical followed by ring closure at the *ortho* position with subsequent dehydrohalogenation. The experimental conditions were such that all of these processes could occur to a small extent which is reflected by the low yield.

Experimental

Benzoyl peroxide (20 g.) was added in 1-g. portions to refluxing trichloroethylene (16.8 moles) over a period of 96 hr. The temperature of the reaction mixture rose from 88 to 100° during this time. The reaction mixture was then flash distilled to remove the unchanged trichloroethylene (9.9 moles). The remainder was heated to 150–160° at atmospheric pressure for 12 hr. and hydrogen chloride was slowly evolved. Distillation at 3 mm. pressure then gave pentachlorobutadiene (0.32 mole), hexachlorobutene (3.0 moles), and 210 ml. of a viscous residue. The final temperatures for vapor and residue were 80 and 110°. 1,2,3,4-Tetrachloronaphthalene (5 g.) was recovered from the residue by filtration. Recrystallization from ethyl ether gave colorless crystals, m.p. 194–200° (lit., 196°,[3] 198°,[4] and 199–200°[5]).

Anal. Calcd. for $C_{10}H_4Cl_4$: C, 45.15; H, 1.52; Cl, 53.33. Found: C, 45.14; H, 1.76; Cl, 53.33.

(1) A. Roedig and R. Kloss, *Chem. Ber.*, **90**, 2902 (1957); O. Simamura and N. Inamoto, *Bull. Chem. Soc. Japan*, **27**, 152 (1954).

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(3) E. G. Turner and W. P. Wynne, *J. Chem. Soc.*, 243 (1941); W. P. Wynne, *ibid.*, 61 (1946).

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Studies on the Leaves of the Family Salicaceae. I. Populin from the Leaves of *Populus grandidentata* and *Populus tremuloides*

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Received February 8, 1962

The isolation of a new glucoside, grandidentatin, from the bark of the bigtooth aspen (*Populus grandidentata*) in small quantities was reported recently.[1] In the course of the determination of the structure of grandidentatin, it was necessary to obtain larger amounts of the new glucoside. Because some of the glucosides of several species of *Salix* and *Populus* occur in both the bark and the leaves of these species, the leaves of bigtooth aspen were suggested as a possible source of grandidentatin in larger amounts. The present paper reports the first studies on the isolation of glucosides from the

(1) I. A. Pearl and S. F. Darling, *J. Org. Chem.*, submitted for publication.

leaves of bigtooth aspen and the related quaking aspen (*P. tremuloides*).

Freshly obtained leaves from a bigtooth aspen felled in July in Appleton, Wisconsin, were extracted with boiling water, and the hot extract was treated with excess basic lead acetate and allowed to stand overnight. The mixture was filtered, and the clear filtrate was deleaded in the usual manner with hydrogen sulfide. The resulting clear aqueous solution was concentrated in a laboratory circulating evaporator under reduced pressure. Shortly after evaporation began, crystals separated in the concentrated liquor. These crystals were identified as populin, the 6-monobenzoate of salicin. The filtrate from these crystals was processed by procedures employed previously for aspen barks.[2] Although many unknown compounds were indicated by chromatography, only salicin was isolated as another identified glucoside from the extract.

The finding of populin in the leaves of *P. grandidentata* was unexpected because earlier studies[2] led us to believe that the barks of the American *Populus* species did not contain populin, and we assumed that the glucoside content of the leaves of a particular species would resemble the glucoside content of the bark of the same species. Subsequently, however, we found populin by Craig machine fractionation of the extractives of *P. grandidentata* bark,[3] thus supporting our original assumption. In order to test this assumption further, we subjected to water extraction the July leaves of *P. tremuloides*, a species whose bark has never yielded populin.[2,4] The hot water extract of this species, when processed in the manner noted for bigtooth aspen leaf extract, yielded crystalline populin, but in somewhat less yield. As in the case of the bigtooth aspen leaf extract, the filtrate from the populin yielded salicin and a similar mixture of unknown compounds. Thus, the leaves of the American quaking aspen (*P. tremuloides*) provide a good source of the 6-monobenzoate of salicin, populin, while the bark of the same species provides a good source of the 2-monobenzoate of salicin, tremuloidin.[5]

To investigate the possibility that the presence of populin in the leaves of these two *Populus* species was a function of the time of collection, leaves of *P. grandidentata* from the same clone were collected in September and in October. Hot water extracts of these two samples of leaves gave essentially the same results as the earlier July leaf extract, indicating that populin exists in the leaves of bigtooth aspen as a product of biosynthesis and not as an intermediate.

Qualitative analysis of the ether-soluble phenolic materials liberated from the lead precipitates from both the bigtooth and quaking aspen leaf extracts indicated the presence of vanillic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, ferulic acid, vanillin, and acetovanillone in both extracts, and syringic acid and syringaldehyde in the bigtooth extract only. This lack of the two syringyl compounds in the quaking aspen leaf extract may be of taxonomic significance.

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(3) I. A. Pearl, O. Justman, D. L. Beyer, and D. Whitney, *Tappi*, submitted for publication.

(4) I. A. Pearl and S. F. Darling, *J. Org. Chem.*, **24**, 1616 (1959).

(5) I. A. Pearl and S. F. Darling, *J. Org. Chem.*, **24**, 731 (1959).

Experimental[6]

Isolation of Populin from Bigtooth Aspen Leaves.—An amount of 1490 g. (oven-dry basis) of leaves freshly obtained from a 13-year-old bigtooth aspen (*Populus grandidentata*) felled in Appleton, Wisconsin, on July 21, 1960, was digested with 30 l. of boiling water and filtered hot through cloth. The hot filtrate was treated with an excess of basic lead acetate, stirred, and allowed to stand overnight. The yellow precipitate was filtered, and the clear filtrate was saturated with hydrogen sulfide, heated to boiling, and filtered. The almost colorless filtrate was concentrated in a laboratory circulating vacuum evaporator. Shortly after evaporation began, crystals separated in the concentrated liquor. Concentration was continued until the concentrated liquor became thick with precipitated crystals. The crystals were filtered and washed with water to yield 10.0 g. of white needles melting at 180–181°. These crystals were recrystallized from water to give needles with unchanged melting point and with specific rotation, infrared absorption spectrum, and R_f values identical with those reported earlier[5] for synthetic populin prepared by the procedure of Richtmyer and Yeakel[7] and for natural populin isolated from *Populus alba* leaves by the procedure of Herberger.[8] A mixed melting point with synthetic populin was not depressed.

Further concentration of the aqueous filtrate yielded another 1.0 g. of populin melting at 178–179°. The total yield of populin amounted to 0.74% on the basis of the original leaf solids.

Further Evaluation of Bigtooth Aspen Leaf Extract.—The concentrated aqueous filtrate from the last populin crystals was evaporated further to 500 ml. and extracted exhaustively with ethyl acetate. The ethyl acetate was filtered to yield 9.7 g. of white crystals melting at 193–194°. These were recrystallized from ethanol to give white crystals of salicin melting at 196–197° and having specific rotation and infrared absorption spectrum identical with those of authentic salicin. The ethyl acetate filtrate was chromatographed at 20° in 10:3:3 butanol–pyridine–water, and the chromatograms were sprayed with the modified silver[5] and diazotized *p*-nitroaniline[9] spray reagents. Spots were located at R_f's 0.60, 0.72, and 0.85 with the silver reagent and at 0.64 (red-violet), 0.79 (violet), and 0.86 (purple surrounded by red-violet) with the diazo reagent. No spots for either grandidentatin or salireposide were found.

The aqueous raffinate from the ethyl acetate extraction was spotted on replicate papers and chromatographed in the butanol–pyridine–water and 8:2:1 ethyl acetate–pyridine–water developers. The chromatograms were sprayed with modified silver, diazotized *p*-nitroaniline, modified aniline hydrogen phthalate,[10] and urea[11] spray reagents. These chromatograms indicated the presence of salicin, sucrose,

(6) All melting points are uncorrected. Infrared absorption spectra were determined by Mr. Lowell Sell of The Institute of Paper Chemistry Analytical Department.

(7) N. K. Richtmyer and E. H. Yeakel, *J. Am. Chem. Soc.*, **56**, 2495 (1934).

(8) J. E. Herberger, *Buchners Report Pharm.*, **51**, 266 (1835).

(9) I. A. Pearl and P. F. McCoy, *Anal. Chem.*, **32**, 1407 (1960).

(10) S. M. Partridge, *Nature*, **164**, 443 (1949).

(11) C. S. Wise, R. J. Dimler, H. A. Davis, and C. E. Rist, *Anal. Chem.*, **27**, 33 (1955).

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.

(12) I. A. Pearl, D. L. Beyer, B. Johnson, and S. Wilkinson, *Tappi*, **40**, 374 (1957).

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

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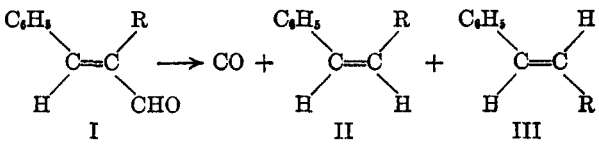
Received February 8, 1962

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.

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(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.