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]

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[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

WILLIAM L. HOWARD AND RONALD E. GILBERT

Organic Basic Research Laboratory, The Dow Chemical Company, Freeport, Texas

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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.

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

IRWIN A. PEARL, STEPHEN F. DARLING,
AND OLIVER JUSTMAN

The Institute of Paper Chemistry, Appleton, Wisconsin

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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

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