equimolar mixture of mono- and dibutylated *t*-butyl crotonates.

Hydrolysis of 7.5 g. of this oil by refluxing with a solution of 10 g. of potassium hydroxide in 40 ml. of aqueous ethanol from 6 hr. afforded 2.0 g. (15% based on *n*-butyl bromide) of crystalline acid melting at 22–24°. Single recrystallization from petroleum ether (b.p. 30–60°) afforded an analytical sample of **2-*n*-butyl-2-butenoic acid,**[15] m.p. 24.5–25.5°, which gave correct analyses for carbon and hydrogen. The infrared spectrum (neat liquid) showed absorptions at 1680 and 1640 cm.$^{-1}$ (α,β-unsaturated carboxylic acid). No vinyl absorptions were observed.

Catalytic hydrogenation of 0.71 g. of 2-*n*-butyl-2-butenoic acid was carried out at room temperature in 50 ml. of ethanol and in the presence of 0.5 g. of Raney nickel (W-5 grade).[11] The resulting **2-butylbutyric acid** distilled at 88–95° (bath temperature)/1 mm., and had $n^{15}\text{D}$ 1.4280. Chlorination with thionyl chloride, followed by treatment with aqueous ammonia, afforded **2-*n*-butylbutyramide,** m.p. 100–101° (lit.,[16] 101–102°), after recrystallizations from water. The amide gave correct analyses for carbon and hydrogen.

Upon distillation of the neutral portion of the hydrolysis products under reduced pressure 3.3 g. (28% based on *n*-butyl bromide) of ***t*-butyl 2,2-di-*n*-butyl-3-butenoate,** b.p. 90–91°/2.5 mm., $n^{16}\text{D}$ 1.4385, was obtained.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89. Found: C, 75.32; H, 11.87.

The infrared spectrum (neat liquid) showed absorptions at 1720 cm.$^{-1}$ (nonconjugated ester) and at 1000 and 910 cm.$^{-1}$ (a vinyl group).

Acknowledgment.—The authors are indebted to Mr. N. Hayakawa, Japan Atomic Energy Institute, for NMR measurements. His assistance is gratefully acknowledged.

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(15) R. Adams and L. J. Roll, *J. Am. Chem. Soc.*, **53**, 3469 (1931). These authors recorded the acid as an oil.

(16) H. S. Raper, *J. Chem. Soc.*, **91**, 1831 (1907).

Improved Production of Phenylchlorocarbene

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McElvain[1] and Breslow[2] generated phenylchlorocarbene by the action of potassium *t*-butoxide on benzal chloride; the carbene, in each case, was trapped *via* addition to ketene acetals. We have prepared adducts I, III, IV, VII, VIII, IX, and X in a similar manner (see Table I). The preparation of II, IV, VI, VIII, and X required the prior synthesis of *p*-methylbenzal chloride, a white, crystalline solid (m.p. 50–51°, from methanol) obtainable through reaction of phosphorus pentachloride and *p*-tolualdehyde.

Production of 1-chloro-1-phenylcyclopropanes by the butoxide α-elimination method is limited. The reaction does not proceed well at temperatures much below 70°, thus precluding the use of butenes as acceptors under simple reaction conditions. Indeed, the attempted synthesis of IX *via* the butoxide method at 0° failed. In no case does the yield exceed 40%, adducts III and IV were obtained in highly impure form, while adduct II could not be prepared in sufficient yield to permit separation from concomitant impurities.[3] In all cases, considerable quantities of quite high-boiling and presumably polymeric materials were formed.

These difficulties may be obviated if methyllithium is employed rather than the butoxide.[5] Adducts II, V, VI, and X were produced in this manner. The methyllithium benzal chloride reaction may be carried out at 0° and gives little polymer, no impurities boiling in the same range as the desired product and higher yields. For example, X was obtained in only 17% yield by the butoxide reaction, but in 42% yield by the methyllithium route. Adduct II, which could not be obtained by the butoxide method, resulted in 21% yield by the methyllithium method. The butene adducts V and VI were also preparable by this method only.

Structures of adducts V, VI, IX, and X are in accord with NMR data. In all pairs the methyl analog exhibits a signal in the region 7.69–7.82 τ, whereas the remainder of the spectrum is identical in shape to that of the unsubstituted adduct.

All adducts possessed an infrared absorption in the region 1030–1000 cm.$^{-1}$. In accord with the literature, the band nearest 1021 cm.$^{-1}$ was considered as characteristic of the cyclopropane ring.[6]

Experimental

Olefins.—1-Hexene and isobutylene were Phillips Petroleum C.p. Tetramethylethylene was prepared by the method of Whitmore.[7] *trans*-Hexene-3 was prepared by the method of Pomeranz.[8] Methylenecyclohexane was prepared by pyrolysis of cyclohexylmethyl acetate at 500° on a glass-packed column.

Benzal chloride was Matheson technical grade, purified by distillation over a tantalum spiral column at 103°/28 mm.

***p*-Methylbenzalchloride.**—An 85-g. sample of phosphorus pentachloride was placed in a two-neck 500-ml. flask, fitted with a dropping funnel and mechanical stirrer. The temperature was kept at 25° by means of a water bath. A 50-g. sample of *p*-tolualdehyde was added dropwise, with stirring over 1 hr. Stirring was continued for 6 hr., care being taken to exclude direct light. The reaction mixture was

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(2) R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

(3) These impurities absorb at 1700–1680 cm.$^{-1}$ in the infrared. Though there is evidence that butoxide can cause elimination in ketene acetal adducts,[1,4] we have treated V for eighteen hours with butoxide in refluxing hexene-1 without effecting any noticeable change. In addition, a prepared mixture of several adducts was not affected by methyllithium at 0°. We conclude that the impurities result from an alternate consumption of benzal chlorides when these are reacted with butoxide in the presence of a poor acceptor olefin. No such impurities were formed when the olefin was a better acceptor or when methyllithium was employed.

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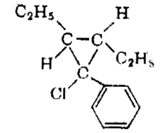
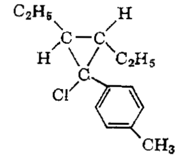
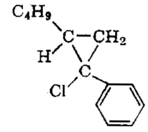
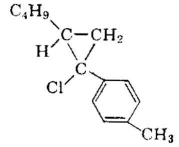
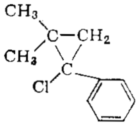
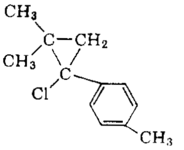
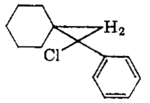
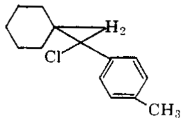
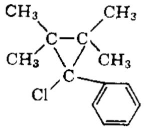
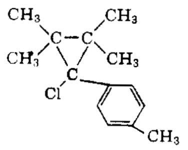
(5) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

(6) L. J. Bellamy, "Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1960, pp. 29f.

(7) F. C. Whitmore and L. Black, *J. Am. Chem. Soc.*, **64**, 1619 (1942).

(8) P. Pomeranz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Natl. Bur. Std.*, **52**, 59 (1954).

TABLE I

No.	Adduct	B.p. (or m.p.), °C.	n^{25}_D	Yield,[a] %	Infrared,[b] cm.$^{-1}$	Calcd.	Found
I		56°/0.025	1.5122	12[g]	1027	C 74.80 H 8.20 Cl 16.99	75.04 8.13 16.71
II		64°/0.025	1.5145	21[e]	1021	Cl 15.92	14.78[f]
III[c]		56–61°/0.075	1.5072	44[g]	1008	C 74.80 H 8.20 Cl 16.99	75.14 8.19 16.50
IV[c]		86–87°/0.25	1.5124	35[g]	1018	C 75.48 H 8.60 Cl 15.92	75.75 8.20 15.45
V		68°/1.5	1.5232	54[e]	1025	Cl 19.62	19.63
VI		57–58°/0.050	1.5230	68[e]	1019	Cl 18.21	18.28
VII		79°/0.20	1.5434	37[g]	1016	C 75.83 H 8.18 Cl 15.99	76.32 7.85 15.87
VIII		95–96°/0.25	1.5445	32[g]	1016	C 76.41 H 8.55 Cl 15.04	76.92 8.30 14.65
IX[d]		(66–67°)	...	40[g]	1026	C 74.80 H 8.20 Cl 16.99	74.86 8.18 17.19
X[d]		(108–109°)	...	17[g] 42[e]	1021	C 75.49 H 8.60 Cl 15.92	75.52 8.97 15.60

[a] Yields reported are for the purified adducts, except adducts III and IV. [b] This is the "cyclopropane" absorption (see text). [c] These adducts were not separated into their isomeric components. [d] Purified by sublimation. [e] Made by methyllithium method. [f] Decomposes upon standing. Attempts to purify this compound by vapor phase chromatography resulted in pyrolysis. Chromatography on alumina destroyed the compound. Distillation under vacuum will not separate the apparent impurity. The 1% error in chlorine analysis is due to the instability of the compound, for a subsequent analysis of the same sample indicated a further loss of chlorine to about 13%. [g] Made by butoxide method.

then poured over water–ice, thoroughly agitated, and the resulting solid was quickly filtered, washed with water, and taken up in ether. The ethereal solution was washed with water, sodium bicarbonate solution, again with water, and dried over sodium sulfate. The ether was removed under reduced pressure, and the solid material recrystallized from the smallest suitable volume of hot methanol. The yield of white crystals melting at 50–51° was 52.0 g. (72%).

Anal. Calcd. for $C_8H_8Cl_2$: Cl, 40.51. Found: Cl, 40.02.

p-Methylbenzal chloride slowly hydrolyzes when exposed to the atmosphere and should be stored under nitrogen in a dark place.

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

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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*

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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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