TABLE I

The nuclear magnetic resonance spectra of **1** and **2** neat with internal tetramethylsilane reference

	β-CH_3	β-H	α-H	—CHO
1	7.90 τ *J* 7.6, 1.8 Hz	3.36 τ 11.4, 7.6 Hz	4.19 τ 11.4, 8.0, 1.8 Hz	−0.04 τ 8.0 Hz
2	8.07 τ *J* 6.7, 1.5 Hz	3.15 τ 15.4, 6.7 Hz	4.01 τ 15.4, 7.6, 1.5 Hz	0.60 τ 7.6 Hz

equilibrium achieved from the crotonates is 83:12:5 for *trans*:*cis*:β, γ at 300° (14).

The formation of *cis*-crotonaldehyde from the *trans*-isomer may be a key step in the photoisomerization of crotonaldehyde to 3-butenal, which is an important step in the photochemical breakdown of this 4 carbon unit (6). The deconjugated isomer is expected to be formed photochemically from the *cis*-isomer rather than from the *trans*-isomer for precedent is available for this preference in the ketone series (8). The ready isomerization of **1** in acid accounts for its absence in normal methods for preparation of crotonaldehyde (15) and for the lack of detection by Blacet *et al.* (1). By extrapolation citral and other naturally occurring α,β-unsaturated aldehydes can be expected to isomerize thermally and with acid. An equilibrium of citral *a* to citral *b* of 61:39 is in fact achieved at 140°.

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Reaction of diphenylphosphine and 1,2-dichlorotetrafluorocyclobutene

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Diphenylphosphine and 1,2-dichlorohexafluorocyclobutene react in a solvent medium of dimethyl formamide to give both the mono (**3**) and 1,2-disubstituted (**2**) derivatives as products. In contrast, these same reactants give entirely different products when the reaction is conducted in the absence of a solvent.

Analytical and spectroscopic data are presented for the proposed structures.

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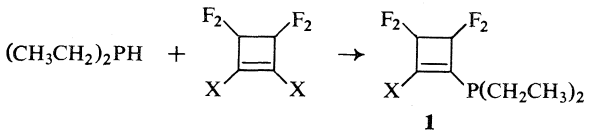
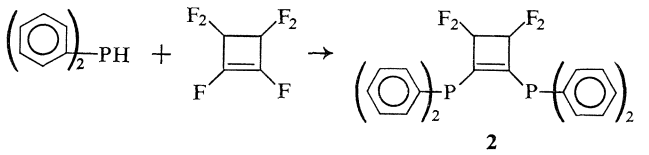
The reactions of secondary phosphines and perhalocyclobutene have been investigated recently (1). While diethylphosphine reacts with either perfluorocyclobutene or 1,2-dichlorotetrafluorocyclobutene to give the monosubstituted tertiary phosphine **1**, diphenylphosphine reacts with perfluorocyclobutene to give only the disubstituted tertiary phosphine **2**. Interestingly, diphenylphosphine did not give an analogous product with 1,2-dichlorotetrafluorocyclobutene,

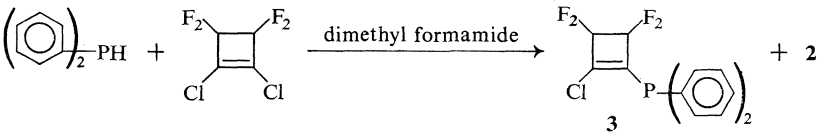


1

where X = Cl or F



2



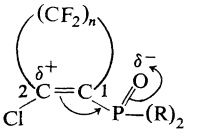
3

but instead hydrogen chloride, trifluorodiphenylphosphorane, and diphenylphosphinic fluoride were found. All of these experiments were carried out in the absence of solvent (neat). The reaction of 1,2-dichlorotetrafluorocyclobutene and diphenylphosphine was of particular interest in view of some recent work which this laboratory has just published (2).

The effect of the reaction medium, in which similar type nucleophilic reactions have been carried out (3), indicates that the judicious choice of a solvent can play a dominant role in product(s) formation. The reason for this is that the chemical potential of the various species involved in the reaction can be altered by the dipolar aprotic solvent (4).

With dimethyl formamide as the solvent, diphenylphosphine and 1,2-dichlorotetrafluorocyclobutene gave both **3** (46.3%) and **2** (20.0%). This result is in contrast to the work of Cullen *et al.* (1), where the reaction was run in the absence of a solvent.

Based on the reactions of phosphites and 1,2-dichlorohexafluorocyclopentene (5), the formation of **2** might not have been predicted. With phosphites as the nucleophile, the 1,2-disubstituted products are exclusively found due to a conjugative effect by the phosphonate group which renders C-2 susceptible to further nucleophilic attack (**4**). Although this electronic effect is not possible with **3**, a 1,2-disubstituted product is still found.



$n = 3$

4

Recent studies involving cyclic perhaloolefins and alkoxides (6, 7) suggest that the products can be predicted on the basis of the stability of the intermediate carbanions formed. Undoubtedly, as illustrated in this and other studies (1, 2, 6–8) the actual product distribution must definitely depend on other factors like ring size, nucleophilicity of the reactant, steric hindrance, polarity of the reaction medium, as well as electronic effects. Much more work is needed before the role of each variable can be deduced, and its role in the mechanistic pathway be understood.

Experimental

The infrared (i.r.) spectra were determined as mineral oil mulls on a Perkin–Elmer model 317 spectrophotometer. Phosphorus nuclear magnetic resonance (n.m.r.) spectra were measured as 10% solutions using triethylphosphate as the reference on a Varian HR-60 instrument.

Preparation of **3** *(2-Chloro-3,3,4,4-tetrafluoro-1-cyclobuten-1-yl)diphenylphosphine and* **2** *(3,3,4,4-Tetrafluorocyclobuten-1,2-ylene)bisdiphenylphosphine*

A solution of 19.5 g (0.1 mole) of 1,2-dichlorotetrafluorocyclobutene and 18.6 g (0.1 mole) of diphenylphosphine (9) in 100 ml of dimethyl formamide was stirred at 65 °C for 10 h, then poured into 300 ml water. The organic materials were extracted twice with 100 ml

ether and the combined ethereal extracts were washed three times with 50 ml portions of water. The ether solution was dried over anhydrous $MgSO_4$ and concentrated to dryness. The crude consisted of solid and an oil. Approximately 10 g of solid (**2**) were filtered off and 16 g of oil (**3**) remained. The oil was distilled at 114–116 °C/0.1 mm and the solid was recrystallized from ethanol and had m.p. 127–127.5 °C (lit. (1), m.p. 129.5–130.5°). A vapor-phase chromatography analysis employing an F and M model 810 equipped with a 3 ft silicon gum rubber column indicated that the crude mixture had at least two other minor components representing less than 5% of the total besides **2** and **3**.

Anal. Calcd. for **3**, $C_{16}H_{10}ClF_4P$: C, 55.76; H, 2.90; Cl, 10.28; P, 8.99. Found: C, 55.36; H, 3.14; Cl, 10.41; P, 8.78.

Infrared spectrum (neat): some of the more significant peaks are 3060w, 1575m, 1480m, 1320s, 1120vs, 1070w, 1030w, 1000m, 860s, 835s, 745s, 693s. Nuclear magnetic resonance: the phosphorus spectrum shows only one peak at +25.1 p.p.m., which is in agreement for a tertiary phosphine (10).

Anal. Calcd. for **2**, $C_{28}H_{20}P_2F_4$: C, 68.03; H, 4.04; P, 12.54. Found: C, 68.29; H, 4.38; P, 12.71.

Infrared spectrum (mull): some of the more significant peaks are 1595w, 1435m, 1375w, 1295s, 1220s, 1155s, 1085s, 1065w, 1025w, 1000w, 830m, 822m, 758m, 740s, 730w, 725m, 694s. Nuclear magnetic resonance: the phosphorus spectrum shows only one peak at 22.7 p.p.m. which is in agreement for a tertiary phosphine (10). A sample of **2** was obtained from Professor W. R. Cullen (1) and it was shown by i.r., ^{31}P n.m.r., and a mixture melting point, to be identical to that obtained in this work.

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7-*O*-β-D-Glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone—a new *C*-methyl flavanone glycoside from Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] roots

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A new *C*-methyl flavanone, 7-*O*-β-D-glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone, has been obtained from healthy Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] root bark in a high yield of 2.6%. Its structure was elucidated by high resolution and mass spectrometry together with a variety of chemical and physical tests and confirmed by synthesis of its methylated aglycone. Pathological testing of this new glucoside against *Poria weirii* Murr. is being undertaken.

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The first new *C*-methyl flavanone, poriol, to be discovered in Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] roots has been described in a previous paper (1). In contrast to poriol, which was obtained in low yield (0.2%) from diseased (*Poria weirii* Murr.) Douglas-fir root bark, the new *C*-methyl flavanone glucoside (**1**) was obtained in high yield (2.6%) from healthy Douglas-fir root bark. The structure of this new *C*-methyl flavanone glucoside (**1**) is proposed as 7-*O*-β-D-glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone.

Flavanone glucoside (**1**) crystallized from an ethyl acetate extract of healthy Douglas-fir root bark. This bark had been previously extracted