Replacement of the hydrochloric acid by acetic acid gave a 74.5% yield of **1** and no **7**, while replacement of the hydrochloric acid by formic acid gave a 67% yield of **1** and a 5% yield of **7**.

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We should like to thank Finkelstein and Brossi (1) for making the details of the procedure for the synthesis of **1** available to us before publication.

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cis-Crotonaldehyde and related compounds

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cis-Crotonaldehyde (**1**) has been prepared as a mixture with *trans*-crotonaldehyde (**2**) by irradiation of **2** with 3000 Å light. The thermodynamic equilibrium value for **1** to **2** was determined to be 1:50. Conditions for attaining this equilibrium and the structural factors contributing to its position are discussed.

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In one reported attempt to prepare *cis*-crotonaldehyde (**1**) by irradiation of an acid solution of *trans*-crotonaldehyde (**2**) no evidence could be found for the formation of **1** (1). The photodecomposition (2–6) and photooxidation (7) of **2** has been studied without reports of the formation of **1**. On the other hand irradiation of *trans*-α,β-unsaturated ketones readily leads to the *cis*-isomers (5, 8, 9). As part of a general study on the chemistry of α,β-unsaturated carbonyl compounds we have investigated the conversion of **2** to **1**.

Irradiation at room temperature of **2** sealed in a 4 mm tube in a Rayonet Srinivasan-Griffin reactor using 16 RPR-3000 Å lamps gave after 4 days a mixture of **1** and **2** in the ratio of 29:71. Further irradiation did not increase the proportion of **1**. Detection of **1** in **2** was possible by nuclear magnetic resonance (n.m.r.) and the spectra of **1** and **2** are given in Table I.[1]

cis-Crotonaldehyde (**1**) was found to be particularly sensitive to acids being converted rapidly with a trace of acid to **2**. The separation of **1** from **2** has as yet been unsuccessful by distillation or vapor-phase chromatography with a variety of columns including DIDP, DNP, Ucon P, silver nitrate-glycerol, DEGS and Poropak Q. Samples collected from the chromatograph (Varian Aerograph A-90P) remained unchanged. Heating samples of **1** and **2** indicated **1** to be also thermally labile with half-life of 2 h at 160°. This value however is a minimum due to the sensitivity of **1** to acid.

The thermodynamic equilibrium of **1** and **2**, attained at room temperature with a trace of dry hydrochloric acid or by heating mixtures to 200 °C for 5 h, contains 2.0% of **1**. No evidence was found for the presence of 3-butenal which would be expected to be less than 0.5% based on the results of Sifniades (11) who found 0.35% of 3-butenal in equilibrium with crotonaldehyde when **1** was heated in the gas phase at 150° and 1% at 210°. For comparison we have determined the acid-catalyzed equilibrium of angelaldehyde with tiglaldehyde to be 1:100 and of *cis*-3-methyl-3-penten-2-one with *trans*-3-methyl-3-pentene-2-one to be 1.5:100.

The marked stability of the *trans*-conjugated forms of these compounds implies a high resonance stabilization in this form. This stabilization apparently is reduced in the *cis* form by distortion from planarity of the carbonyl group of the conjugated system. The importance of this destabilizing interaction is emphasized in angelaldehyde and *cis*-3-methyl-3-pentenoate where the stable isomer involves a *cis* arrangement of two methyl groups rather than a *cis* arrangement of a methyl and the smaller formyl or acetyl groups (the conformational free energy difference $-\Delta G$ for the formyl group on a cyclohexane ring is 1.35 (12) compared to 1.7 for methyl (13)).

The conjugative stabilization in esters is expected to be less than that for ketones and aldehydes and this is supported by the fact that the

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[1] The spectrum of **2** is reported in ref. 10.

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	3.36 τ	4.19 τ	-0.04 τ
	J 7.6, 1.8 Hz	11.4, 7.6 Hz	11.4, 8.0, 1.8 Hz	8.0 Hz
2	8.07 τ	3.15 τ	4.01 τ	0.60 τ
	J 6.7, 1.5 Hz	15.4, 6.7 Hz	15.4, 7.6, 1.5 Hz	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,