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Photochemical Transformations. XI. Photochemical and Thermal Rearrangements of Some β-Substituted Allylic Systems[1]

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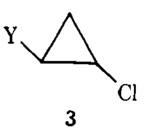
The photochemistry of β-chloro- and β-phenylcinnamyl and -crotyl chlorides has been investigated. These compounds, under both sensitized and direct irradiation, undergo cis–trans isomerizations and allylic rearrangements. The photostationary states contain substantial amounts of the thermally less stable secondary isomers. Sensitized irradiation of β-chlorocinnamyl *p*-toluenesulfonate and methanesulfonate also resulted in cis–trans isomerizations and rearrangements. Quantum yield and quenching results are reported and possible reaction mechanisms are discussed.

As reported earlier,[2] allyl chloride is readily transformed by triplet photosensitization to cyclopropyl chloride, and this photosensitized cyclization is a fairly general reaction. Thus, for example, crotyl chloride (1-Me) rearranges to a mixture of *cis-* and *trans-*2-chloro-1-methylcyclopropane (2-Me and 3-Me, respectively), cinnamyl chloride (1-Ph) to *trans*-2-chloro-1-phenylcyclopropane (3-Ph), and 2-methylallyl chloride (4) to 1-chloro-1-methylcyclopropane (5). α-Methylallyl chloride (6-Me), the allylic isomer of **1**, also is photoisomerized to a mixture of 2-Me and 3-Me, and α-phenylallyl chloride (6-Ph) to 3-Ph, all *via* triplet intermediates.[2] Accompanying these 1,2-chlorine migration cyclizations is a generally somewhat faster allylic (1,3) migration. Thus, 1-Me and 6-Me suffer photosensitized isomerization to a mixture of the two, and 1-Ph is transformed to 6-Ph. Similar results were also noted for 1,3-dichloropropene (1-Cl) and 3,3-dichloropropene (6-Cl), which were also transformed to each other as well as photorearranged and cyclized to 2-Cl and 3-Cl.[2]

$YCH{=}CHCH_2Cl$

1

2



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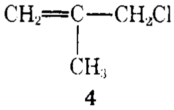
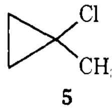


$CH_2{=}C(CH_3){-}CH_2Cl$

4



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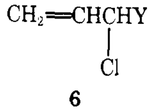
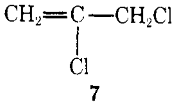


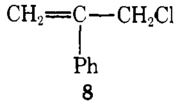
$CH_2{=}CHCH(Cl)Y$

6



$CH_2{=}C(Cl){-}CH_2Cl$

7



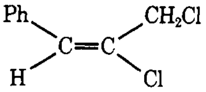
$CH_2{=}C(Ph){-}CH_2Cl$

8

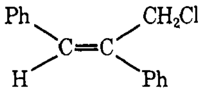
In view of these results, it was surprising that β-chloroallyl chloride (7) and β-phenylallyl chloride (8) were apparently inert to photosensitization, neither giving detectable amounts of the anticipated cyclopropane, when irradiated in acetone–acetonitrile solution with a Hanovia 450-W Model L lamp in thin-walled Pyrex tubes, the conditions used routinely for the photocyclization rearrangements.[2] As the allylic rearrangements of 7 and 8 (as well as cis–trans isomerizations) are degenerate processes and therefore hidden, we were unable to learn whether the photoinertness was complete or was limited to the 1,2-sigmatropic rearrangement–cyclization.

Results

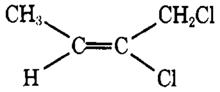
We, therefore, have now prepared β-chlorocinnamyl chlorides (**9**) and β-phenylcinnamyl chlorides (**10**), and the analogous crotyl chlorides **11** and **12**, where one can observe allylic rearrangements, cis–trans isomerizations, and allyl to cyclopropyl rearrangements, to the extent that any of these occur upon irradiation. Our preparative and isolation methods led to materials (which were used as reagents for photoreactions) which were 100% (*E*)-**9** (β-chloro-*cis*-cinnamyl chloride), 100% (*E*)-**10** (β-phenyl-*trans*-cinnamyl chloride), 98% (*E*)-**11** (β-chloro-*cis*-crotyl chloride), and a



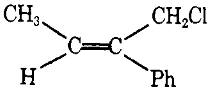
(*E*)-**9**



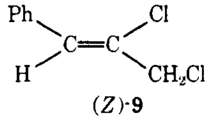
(*Z*)-**10**



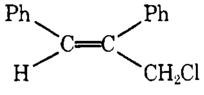
(*E*)-**11**



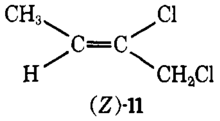
(*Z*)-**12**



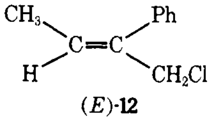
(*Z*)-**9**



(*E*)-**10**



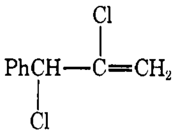
(*Z*)-**11**



(*E*)-**12**

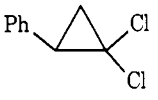
mixture of 17% of (*E*)-**12** (*β*-phenyl-trans-crotyl chloride) and 83% of (*Z*)-**12** (*β*-phenyl-*cis*-crotyl chloride).

Upon irradiation of these substances in acetonitrile–acetone solvent sensitizer, each was converted fairly rapidly toward a "photostationary" state of *E* and *Z* isomers. The compositions of these mixtures are described in the Experimental Section; in each case the cis cinnamyl or cis crotyl isomer predominated. Accompanying the cis–trans interconversion, but proceeding at about one-third the rate, was the photochemical allylic rearrangement. Thus, irradiation of a 0.5 *M* solution of **9** for 72 hr led to complete transformation to the allylic isomer, *β*-chloro-*α*-phenylallyl chloride (**13**), without any allyl to cyclopropyl rearrangement to **14** being observed, even on longer irradiation. Irradiation of **13** gave neither cyclization to **14** nor formation of the primary chlorides **9** upon irradiation, within our ability to detect them by pmr analysis. Of possible synthetic importance is the fact that **13** is the "stable" isomer in the **9** ↔ **13** photoequilibration, while in a ferric chloride catalyzed ground-state equilibration **13** is converted completely to **9**. Thus the photochemical isomerization is a useful synthetic procedure for the secondary isomer **13** from the readily available **9**.



$$\mathrm{PhCH(Cl){-}C(Cl){=}CH_2}$$

13



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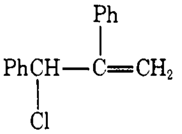
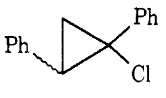


$$\mathrm{PhCH(Cl){-}C(Ph){=}CH_2}$$

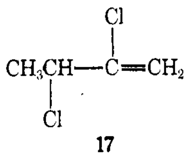
15



16

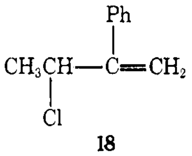
Similarly, irradiation of *β*-phenylcinnamyl chloride (**10**) led to a mixture rich (79%) in the secondary allylic isomer **15**, while ferric chloride catalyzed treatment gave substantially pure primary isomer **10**. The ground-state results on the cinnamyl systems are consistent with those anticipated,[3] while the photochemical results (secondary isomer more photo-"stable") are consistent with those observed earlier[2b] with cinnamyl chloride itself. We rationalize these results on the basis that the more highly conjugated primary isomers **9** and **10** have lower singlet energies and therefore probably lower triplet energies than their secondary isomers **13** and **15**, and that the photoisomerization proceeds to the less conjugated system. Put another way, the triplets of **13** and **15** might be quenched by **9** and **10**, respectively, so that the **9** to **13** reaction (and that of **10** to **15**) would be expected to be more important than the corresponding reverse reactions. An obvious alternative is that energy transfer from sensitizer to the primary isomer is more efficient than that to the secondary isomer.

In the crotyl systems, irradiation of either **11** or its isomer **17** led to a photostationary state mixture containing 70% of **11** and 30% of **17**, while that of either **12** or **18** gave a mixture containing 83% of **12** and 17% of **18**. The corresponding ground-state equilibrations gave mixtures comprising 85% of **11** and 15% of **17** and 76% of **12** and 24% of **18**, respectively.



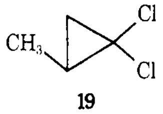
$$\mathrm{CH_3CH(Cl){-}C(Cl){=}CH_2}$$

17



$$\mathrm{CH_3CH(Cl){-}C(Ph){=}CH_2}$$

18



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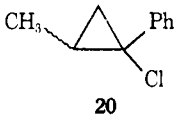
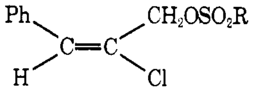


20

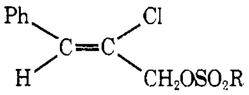
In none of the irradiations was any of the cyclopropanes **14**, **16**, **19**, or **20** detected. In order to test the possibility that the cyclopropanes might be formed, but somehow be unstable to the reaction conditions, **14** and **19** were prepared and irradiated in acetone–acetonitrile (λ >270 nm). Both substances were completely stable.

Our previous results[2] had indicated that all of the processes investigated were reactions involving triplet sensitization, but Bohlmann and his coworkers[4] have reported that a number of allylic chlorides conjugated with alkynyl groups do undergo nonstereospecific photocyclization–rearrangements to alkynylcyclopropyl chlorides upon direct irradiation in nonpolar solvents, apparently *via* singlet intermediates. We thought that perhaps **9** and **10**, which have conjugation of the allylic double bond with aromatic rings or with an aromatic ring and a chlorine atom, might similarly undergo cyclization upon direct irradiation. However, a 120-hr irradiation of (*E*)-**9** in hexane at 300 nm produced no cyclopropane, but only slow cis–trans isomerization and allylic rearrangement to give 79% of (*E*)-**9**, 9% of (*Z*)-**9**, and 12% of **13**. A similar irradiation of (*E*)-**10** produced 25% of the allylic isomer **15**, as well as 15% of (*Z*)-**10**, and again no cyclopropane was formed. It is of interest that Bohlmann did not observe allylic rearrangement in his work.[4]

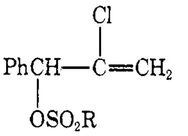
Cookson and coworkers[5] have reported that cinnamyl benzoate and acetate photoisomerize to the secondary *α*-phenylallyl esters with cinchonidine sensitizers. The reaction with the benzoate ester has also been shown[2b] to proceed with acetone sensitization, but cyclization rearrangement was not observed. Sulfonate esters of allylic alcohols are notoriously unstable,[6] but, owing to the *β*-chlorine atom, the thermal reactivity of esters of *β*-chlorocinnamyl alcohol might be expected to be reduced. Both the methanesulfonate ester ((*E*)-**21**-Me) of *β*-chloro-*cis*-cinnamyl alcohol and the *p*-toluenesulfonate ester ((*E*)-**21**-Tl) were prepared and were reasonably stable at room temperature. Irradiation of these esters in acetone–acetonitrile gave a rapid cis–trans photoisomerization to a mixture containing 33–35% of the (*Z*)-**21** species, and a slower photoallylic rearrangement. After 70 hr, **21**-Me was converted to 23% of **22**-Me, and **21**-Tl to about 53% of **22**-Tl.[7] No cyclopropane was noted in the irradiation product.[8]



(*E*)-**21**



(*Z*)-**21**



$$\mathrm{PhCH(OSO_2R){-}C(Cl){=}CH_2}$$

22

Me, R = CH_3
Tl, R = $C_6H_4CH_3$-*p*

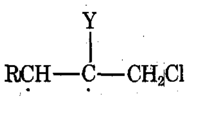
Mechanistic Studies. Although there are examples of photochemical 1,3 (allylic) migrations of a large variety of groups including acyl,[9] alkyl,[10] allyl,[5] phenyl,[11] benzyl,[12] vinyl,[11b,13] boron,[14] and halogen,[2,4] mechanistic details of many of these are unclear. As the allylic rearrangement of **9** and **10** proceeded upon direct irradiation as well as in solutions containing acetone, we began our quantum yield and quenching studies with these compounds. In 0.2 *M* allyl chloride solutions in acetonitrile, the quantum yield for rearrangement of **9** to **13** was found to be 0.016 (a Rayonet photoreactor with 300-nm lamps was used for all quantitative studies) and for that of **10** to **15** was 0.025. Quenching experiments for the **9** → **13** transformation with 1,3-cyclohexadiene gave a Stern–Volmer plot with a slope of 4 (quantum yield reduced by 50% at 0.5 *M* diene). As this low value implies either that the triplet state of the diene is higher in energy than that of the triplet state of **9** or that the singlet state is being quenched,[15] we then looked at similar quenching of acetone solutions of **9**. Our results clearly exclude the first alternative. Thus, the quantum yield for **9** → **13** interconversion of a 0.25 *M* solution of **9** in 20% acetone in acetonitrile was found to be 0.24. The reaction was half-quenched with diene concentrations of about 0.002 *M*. A plot of ϕ_0/ϕ *vs.* diene concentration[16] was linear out to about 0.1 *M* diene, but at higher diene concentrations the slope fell off rapidly. This suggests that the allylic rearrangement proceeds *via* both singlet and triplet states of **9**, with the reaction involving the triplet being substantially more efficient. The data also show that, in the direct irradiation process (in acetonitrile), the singlet produced by direct light absorption proceeds to product without crossing to the triplet, and suggest, as well, that (in acetone) about 7% of the product comes from direct absorption of light by **9** and subsequent product formation, and 93% arises *via* acetone triplets. In direct irradiation, cis–trans isomerization occurs slowly relative to that in the triplet process, and although such a process might be occurring from the singlet state, as in stilbene photochemistry,[17] we cannot rule out the possibility of isomerization arising as a consequence of the photoallylic rearrangement equilibration.

Similarly ϕ for the unsensitized transformation of **10** to **15** (in acetonitrile) was found to be 0.025, while that in acetone–acetonitrile was found to be 0.086 (0.25 *M* **10**). Quenching of the sensitized reaction gave a second-order Stern–Volmer[16] plot which was linear with a slope of 53 at low concentrations (2×10^{-5} to 0.02 *M*) of diene and which fell off at higher concentrations of diene to a line with almost zero slope. Thus again, both singlet and triplet noninterconvertible product progenitors seem required by the data with about one-third of the reaction in the solvent/sensitizer system used proceeding *via* the singlet and two-thirds *via* the triplet in this case. These values presumably reflect relative absorbances of **9** and/or **10** and acetone. Use of a sensitizer such as acetophenone and longer wavelength light would probably give increased efficiencies for the sensitized reaction, as it would cut down on direct irradiation processes, and thus give better "Stern–Volmer" plots. Finally, quantum yields for the sensitized transformations of **11** to **17** and of **12** to **18** were found to be 0.073 and 0.042, respectively, and quenching of the latter transformation gave a linear "second-order" Stern–Volmer plot with a slope of 250 over the range 0.0002–0.07 *M* diene.

Discussion

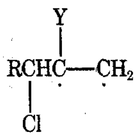
In the previous papers on related rearrangements from this laboratory,[2] a number of detailed mechanistic paths were proposed which were consistent with the data presented. One of these involved homolytic cleavage of the allyl chloride carbon–chlorine bond, followed by recombination. This certainly is a possibility here, but is somewhat unattractive in view of our failure to see other products of free-radical intermediates. Thus, while the allylic radical is relatively unreactive, we would expect to find evidence for its dimerization or for its combination with radicals formed by abstraction of hydrogen atoms from solvent by chlorine atoms[2b] or by addition of chlorine atoms to the allylic double bond.[18]

A second alternative involved the intermediacy of a triplet biradical, and in the present cases might include the corresponding singlet biradicals as well. It was suggested that such biradicals **23** might be anticipated to suffer 1,3-sigmatropic rearrangement to radicals **24** followed by (or in concert with) double bond reconstitution to give allylic isomers or a 1,2 rearrangement to give 1,3-biradicals **25** followed by (or in concert with) ring closure to give cyclopropane. The stereoselectivity noted in the cyclopropane formation[2b,19] set serious boundaries on the latter path. If such biradicals are indeed intermediates, one must explain why the formation of **25** proceeds efficiently ($\phi \sim 0.1$) when Y is hydrogen or alkyl,[2b,18c] with R variable, but not at all when Y is chlorine or phenyl. There is, of course, conjugation energy lost in the **23** to **25** transformation, but this is true as well, although to a lesser extent,[20] for the Y = alkyl cases. The fact that the sulfonate esters show reactions similar to those of the chlorides makes the radical recombination or biradical paths less attractive, assuming that reaction paths identical with those of the chlorides are traversed.



$\underset{\cdot}{\mathrm{RCH}}-\overset{\overset{\mathrm{Y}}{|}}{\underset{\cdot}{\mathrm{C}}}-\mathrm{CH_2Cl}$

23



$\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{RCH}}\overset{\overset{\mathrm{Y}}{|}}{\underset{\cdot}{\mathrm{C}}}-\underset{\cdot}{\mathrm{CH_2}}$

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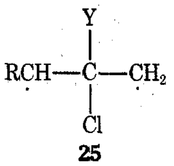
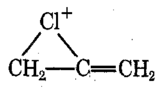


$\underset{\cdot}{\mathrm{RCH}}-\overset{\overset{\mathrm{Y}}{|}}{\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{C}}}-\underset{\cdot}{\mathrm{CH_2}}$

25



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It has also been suggested[2] that the rearrangements involve carbenium ion–anion pairs in which the cation is of the ground electronic state, but vibrationally excited. Olah[22] has shown that 2-chloroallyl cation does not exist in superacid solution, but instead the isomer **26** is stable. Although an analogous situation does not obtain with methyl-substituted 2-chloroallyl cations,[22] species related to **26** may exist in our systems and may fail to rearrange to chlorocyclopropane upon attack by chloride ion. Similar effects might be expected for 2-phenylallyl cations, but not for 2-alkylallyl ones. The photoisomerization of the sulfonate esters **21** to **22** also seems consistent with the carbenium ion process, but the possibility of a concerted [3.3] sigmatropic (photo-Claisen) or of a [1.3] sigmatropic rearrangement also remains. Labeling experiments and stereochemical studies are needed to define these reactions better.

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer. Infrared spectra were run in carbon tetrachloride, using either a Perkin-Elmer Model 337 or Model 137 spectrophotometer. Mass spectra were obtained on a Varian MAT Model CH-7 spectrometer. Analyses of some experiments were performed by gas chromatography (gc) using a Varian Aerograph Model A-90 P-3 instrument. Preparative separations were carried out on an Aerograph Autoprep Model A-700 gas chromatograph. Irradiations were performed using one of two procedures. Method A involved irradiation of 0.5 *M* solutions of each compound in question in acetone-d_6–acetonitrile-d_3 (1:4, v/v, unless specified otherwise) in thin-walled Pyrex tubes (nmr probes) following deaeration with nitrogen for 1 hr at −20°. For these irradiations, a Hanovia 450-W mercury arc lamp (Engelhardt-Hanovia, Inc., Newark, N.J., Model L-679A-36) inserted into a water-cooled quartz-immersion probe was employed. Method B was used for quantitative experiments and involved degassing 3.0-ml sample solutions in preconstricted 13 × 100 mm Pyrex test tubes on a vacuum line with five freeze–pump–thaw cycles and sealing at pressures less than 10^{-5} Torr. The sealed tubes for any single experiment were irradiated in parallel with cyclopentanone actinometer solutions[23] in a merry-go-round photolysis apparatus, using a Rayonet RPR-208 photochemical reactor equipped with 300-nm lamps (The New England Ultraviolet Co., Middletown, Conn.). All quantum yields obtained by these experiments were corrected for back reaction.[24]

(*E*)-*β*-Phenylcinnamyl alcohol was synthesized as described elsewhere.[25]

(*E*)-*β*-Phenylcinnamyl chloride (10) was synthesized using a general procedure devised by Collington and Meyers,[26] and exhibited properties identical with those previously reported:[25] pmr (CCl_4) δ 7.02–7.23 (m, 10 H), 6.70 (t, *J* = 0.5 Hz, 1 H), 4.29 (d, *J* = 0.5 Hz, 2 H).

2,3-Diphenyl-3-chloropropene (15) was prepared from the alcohol using a general method described by Young.[27] Bulb-to-bulb distillation at reduced pressure in a "Kugel Rohr Oven" (131° (2.8 Torr)) gave a 65% yield of **15**: pmr (CCl_4) δ 6.8–7.1 (m, 10 H), 5.88 (s, 1 H), 5.23 (d, *J* = 0.5 Hz, 1 H), 5.19 (d, *J* = 0.5 Hz, 1 H).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.72. Found: C, 78.76; H, 5.78.

(*E*)-*β*-Chlorocinnamyl alcohol was prepared as described elsewhere.[28]

(*E*)-*β*-Chlorocinnamyl chloride (9) was obtained from the alcohol as previously described for *β*-phenylcinnamyl chloride. Distillation at reduced pressure (94–95° (2.5 Torr); lit.[29] 109–110° (4 Torr)) resulted in a 70% yield of (*E*)-**9**: pmr (CCl_4) δ 6.95–7.95 (m, 5 H), 6.35 (s, 1 H), 3.88 (s, 2 H).

3-Phenyl-2,3-dichloropropene (13) was prepared as previously described for 2,3-diphenyl-3-chloropropene. Purification by bulb-to-bulb distillation at reduced pressure (89–90° (1.8 Torr)) resulted in a 43% yield of **13**: pmr (CCl_4) δ 6.95–7.30 (m, 5 H), 5.52 (s, 1 H), 5.50 (d, *J* = 2.0 Hz, 1 H), 5.22 (d, *J* = 2.0 Hz, 1 H).

Anal. Calcd for $C_9H_8Cl_2$: C, 57.78; H, 4.31. Found: C, 57.68; H, 4.44.

(*E*)-*β*-Chlorocrotyl alcohol was prepared as described elsewhere.[28]

(*E*)-*β*-Chlorocrotyl chloride (11) was prepared from the alcohol as described for *β*-phenylcinnamyl chloride. Purification was accomplished by gc (25% Carbowax 20M on Chromosorb P at 150°, 12 ft × 0.375 in. Al column). The pure dichloride exhibited properties identical with those previously reported:[30] pmr (CCl_4) δ 5.89 (q, *J* = 6.5 Hz, 1 H), 4.08 (d, *J* = 0.5 Hz, 2 H), 1.63 (d of d, *J* = 6.5, and 0.5 Hz, 3 H).

2,3-Dichloro-1-butene (17) was prepared as described for 2,3-diphenyl-3-chloropropene. Purification was accomplished by gc (25% Carbowax 20M on Chromosorb P at 150°, 12 ft × 0.375-in. Al column): pmr (CCl_4) δ 5.14 (d, *J* = 1.5 Hz, 1 H), 4.85 (d, *J* = 1.5 Hz, 1 H), 4.37 (q, *J* = 6.5 Hz, 1 H), 1.21 (d, *J* = 6.5 Hz, 3 H).

Anal. Calcd for $C_4H_6Cl_2$: C, 36.68; H, 4.62. Found: C, 36.47; H, 4.73.

***β*-Phenylcrotonaldehyde** was prepared as described elsewhere.[31]

***β*-Phenylcrotyl alcohol** was prepared from the aldehyde as described for *β*-phenylcinnamyl alcohol. Distillation at reduced pressure (101–102° (2.8 Torr)) gave a mixture of the two isomeric alcohols, which was used in the next step without further characterization.

***β*-Phenylcrotyl chloride (12)** was prepared as described for *β*-phenylcinnamyl chloride. Distillation at reduced pressure gave a mixture of *Z* and *E* isomers (83:17, respectively): pmr (CCl_4) δ 7.15 (m, 5 H), 5.76 (q, *J* = 6.0 Hz, 1 H), 4.14 (d, *J* = 1.0 Hz, 2 H), 1.28 (d of d, *J* = 6.0 and 1.0 Hz, 3 H).

Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.04; H, 6.66. Found: C, 72.19; H, 6.74.

3-Chloro-2-phenyl-1-butene (18) was prepared as described for 2,3-diphenyl-3-chloropropene and was obtained in a 40% yield by distillation at reduced pressure (96–98° (2.5 Torr)): pmr (CCl_4) δ 7.25 (m, 5 H), 5.35 (d, *J* = 0.5 Hz, 1 H), 5.21 (d, *J* = 0.5 Hz, 1 H), 4.95 (q, *J* = 7.0 Hz, 1 H), 1.47 (d, *J* = 7.0 Hz, 3 H).

Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.04; H, 6.66. Found: C, 72.12; H, 6.75.

1,1-Dichloro-2-phenylcyclopropane[32] **(14)** and **1,1-dichloro-2-methylcyclopropane**[33] **(19)** were synthesized as described elsewhere.

Irradiation of *β*-Chlorocinnamyl Chloride ((*E*)-9) and 3-Phenyl-2,3-dichloropropene (13) in Acetone–Acetonitrile. *β*-Chlorocinnamyl chloride (0.094 g, 0.5 mmol) was diluted with 0.8 ml of acetonitrile-d_3 and 0.2 ml of acetone-d_6 and placed in a Pyrex nmr tube. The sample was handled as outlined in method A, and irradiated for a total of 100 hr, with the reaction progress monitored by pmr. After 6 hr of irradiation, cis–trans isomerization became evident and a photostationary mixture composition of 64% of (*E*)-**9** and 36% of (*Z*)-**9** was determined. After 76 hr no further change in the pmr spectrum was noted, and it was determined that 100% conversion to the allylic isomer **13** had occurred. No evidence of cyclization was observed.

Similar treatment of 3-phenyl-2,3-dichloropropene (**13**) resulted in no change in the pmr spectrum, even after 100 hr of irradiation.

Ferric Chloride Isomerization of *β*-Chlorocinnamyl Chloride (9) and 3-Phenyl-2,3-dichloropropene (13). 3-Phenyl-2,3-dichloropropene (1.0 g, 5.3 mmol) was diluted with 4.0 ml of spectroquality cyclohexane, to which a trace of ferric chloride has been added. The solution was heated at reflux for 20.5 hr, after which pmr analysis indicated 100% conversion to the primary isomer **9** had occurred.

Similar treatment of *β*-chlorocinnamyl chloride (**9**) led to no detectable formation of the secondary isomer **13**, even after 23 hr of reflux.

Irradiation of *β*-Phenylcinnamyl Chloride ((*E*)-10) and 2,3-Diphenyl-3-chloropropene (15) in Acetone–Acetonitrile. *β*-Phenylcinnamyl chloride (0.115 g, 0.5 mmol) was diluted with 0.8 ml of acetonitrile-d_3 and 0.2 ml of acetone-d_6 and placed in a Pyrex nmr tube. The sample was handled as outlined in method A, with the progress of the reaction being monitored by pmr. After 3 hr of irradiation cis–trans isomerization became evident, and a photostationary mixture composition of 6% of (*E*)-**10** and 94% of (*Z*)-**10** was determined after 12 hr. At the end of 23.5 hr, no further changes in the pmr spectrum could be detected and the product mixture was determined to consist of 27% of **10** and 73% of **15**.

Similar treatment of 2,3-diphenyl-3-chloropropene (**15**) produced a mixture of 28% of **10** and 72% of **15**.

Ferric Chloride Isomerization of *β*-Phenylcinnamyl Chloride (10) and 2,3-Diphenyl-3-chloropropene (13). 2,3-Diphenyl-3-chloropropene (1.0 g, 4.4 mmol) was treated as previously described for 3-phenyl-2,3-dichloropropene. After the solution was heated at reflux for 24 hr, pmr analysis indicated 100% conversion to the primary isomer **10** had taken place.

Similar treatment of **10** led to no detectable formation of the secondary isomer **13**.

Irradiation of *β*-Chlorocrotyl Chloride ((*E*)-11) and 2,3-Dichloro-1-butene (12) in Acetone–Acetonitrile. *β*-Chlorocrotyl chloride (0.066 g, 0.5 mmol) was diluted with 0.8 ml of acetonitrile-d_3 and 0.2 ml of acetone-d_6. The sample was then handled as outlined in method A. Pmr analysis indicated that cis–trans isomerization had reached a photosteady composition of 78% of (*Z*)-**11** and 22% of (*E*)-**11** after 12 hr. After 96 hr, no further changes in the pmr spectrum were detected, and it was determined that the product mixture consisted of 30% of **17** and 70% of **11**.

Similar treatment of **17** produced an identical mixture.

Ferric Chloride Isomerization of *β*-Chlorocrotyl Chloride (11) and 2,3-Dichloro-1-butene (17). *β*-Chlorocrotyl chloride (1.0 g, 7.6 mmol) was treated as previously described for 3-phenyl-2,3-dichloropropene. After the solution was heated at reflux for 24 hr, pmr analysis indicated that the product mixture consisted of 85% of **11** and 15% of **17**.

Similar treatment of **17** produced an identical mixture.

Irradiation of *β*-Phenylcrotyl Chloride (12) and 2-Phenyl-3-chloro-1-butene (18). *β*-Phenylcrotyl chloride (0.083 g, 0.5 mmol) was diluted with 0.8 ml of acetonitrile-d_3 and 0.2 ml of acetone-d_6, and the solution was handled as outlined in method A. Cis–trans isomerization was detectable by pmr analysis after 2 hr, leading to a photostationary mixture of 68% (*Z*)-**12** and 32% of (*E*)-**12** after 9.5 hr. After irradiation for 40 hr, no further changes in the pmr spectrum were detected, and it was determined that the product mixture consisted of 83% of **12** and 17% of **18**.

Similar treatment of **18** produced a mixture containing 79% of **12** and 21% of **18**.

Ferric Chloride Isomerization of *β*-Phenylcrotyl Chloride (12) and 2-Phenyl-3-chloro-1-butene (18). *β*-Phenylcrotyl chloride (1.0 g, 6.1 mmol) was treated as previously described for 3-phenyl-2,3-dichloropropene. Analysis by pmr indicated that the product mixture consisted of 76% of **12** and 24% of **18**.

Similar treatment of the allylic isomer **18** led to an identical product mixture.

Irradiation of 1,1-Dichloro-2-methylcyclopropane (19) and 1,1-Dichloro-2-phenylcyclopropane (14) in Acetone–Acetonitrile. A solution of 1,1-dichloro-2-methylcyclopropane (0.094 g, 0.5 mmol) in 0.8 ml of acetonitrile-d_3 and 0.2 ml of acetone-d_6 was treated as described for the preceding allylic halides. No observable change in the pmr spectrum could be detected, even after 120 hr of irradiation. 1,1-Dichloro-2-phenylcyclopropane (**14**), treated similarly, produced the same result.

Direct Irradiation of β-Phenylcinnamyl Chloride (10) and β-Chlorocinnamyl Chloride (9) in Hexane. β-Phenylcinnamyl chloride (0.115 g, 0.5 mmol) was diluted with 1.0 ml of hexane and placed in a Pyrex nmr tube, and the sample was handled as described in method A. After irradiation for 120 hr, pmr analysis indicated that the product mixture contained 25% of **15** and 75% of **10** (15% of (*Z*)-**10** and 85% of (*E*)-**10**).

Similar treatment of **9** produced a mixture containing 12% of **13** and 88% of **9** (9% (*Z*)-**9** and 91% (*E*)-**9**).

β-Chlorocinnamyl *p*-toluenesulfonate (21-Tl), mp ~15°, was prepared according to the general procedure of Marvel and Sekera.[34] The compound obtained was stable in solutions kept below room temperature. For this reason, the compound was not further characterized: pmr (acetone-d_6) δ 7.0–7.9 (m, 9 H), 6.7 (s, 1 H), 4.15 (s, 2 H), 2.1 (s, 3 H).

β-Chlorocinnamyl methanesulfonate (21-Me), mp ~3°, was prepared according to the general method of Marvel and Sekera.[35] For the same reason cited above, this compound was not further characterized: pmr (acetone-d_6) δ 7.2–7.8 (m, 5 H), 6.8 (s, 1 H), 4.2 (s, 1 H), 3.0 (s, 3 H).

Irradiation of β-Chlorocinnamyl *p*-Toluenesulfonate (21-Tl) and Methanesulfonate (21-Me) in Acetone–Acetonitrile. β-Chlorocinnamyl *p*-toluenesulfonate (0.161 g, 0.5 mmol) was dissolved in 0.8 ml of acetonitrile-d_3 and 0.2 ml of acetone-d_6, taking care that the solution was kept below room temperature, and the sample was handled as described in method A. Irradiation was performed in a water bath held between 12 and 15° to minimize thermal reactions.[36] After 70 hr of irradiation, it was determined by pmr analysis that 53% conversion to the allylic isomer (**22-Tl**) had taken place.

Similar treatment of the methanesulfonate (**21-Me**) resulted in a 23% conversion to the allylic isomer (**22-Me**), as determined by pmr analysis.

Quantum Yield Determination for β-Chlorocinnamyl Chloride (9) and β-Phenylcinnamyl Chloride (10) in Acetonitrile (Direct). β-Chlorocinnamyl chloride (0.919 g, 4.91 mmol) was diluted to 25.0 ml with acetonitrile. Four 3.0-ml aliquots were added to four Pyrex test tubes and the samples were handled as outlined in method B. Work-up following irradiation consisted of solvent removal and dilution of the product mixture with 1.0 ml of a 0.2 *M* solution of cyclohexane (internal standard) in carbon tetrachloride. After 47.5 hr of irradiation, the first tube contained 3.6% of **13** ($\phi = 0.014$). After 72 hr of irradiation, the second tube contained 6.1% of **13** ($\phi = 0.018$). After 144 hr of irradiation, the third tube contained 9.1% of **13** ($\phi = 0.018$). After 219 hr of irradiation, the fourth tube contained 15.9% of **13** ($\phi = 0.015$).

β-Phenylcinnamyl chloride (**10**) was treated similarly. After 49 hr of irradiation, the product mixture contained 5.1% of **15** ($\phi = 0.025$). After 100 hr of irradiation, the product contained 9.6% of **15** ($\phi = 0.025$).

Quantum Yield Determination of β-Phenylcinnamyl Chloride (10) and β-Chlorocinnamyl Chloride (9) in Acetone–Acetonitrile. β-Phenylcinnamyl chloride (0.363 g, 1.59 mmol) was diluted to 6.0 ml with acetone–acetonitrile solution, and this was divided between two preconstricted Pyrex test tubes. The samples were then handled as outlined in method B. After 49.1 hr of irradiation and work-up as described above, one of the tubes contained 17.4% of **15** ($\phi = 0.087$), while the other contained 17.2% of **15** ($\phi = 0.086$).

β-Chlorocinnamyl chloride (**9**) was treated similarly, and after 19 hr of irradiation, one of the tubes contained 10.9% of **13** ($\phi = 0.245$), while the other contained 10.7% of **13** ($\phi = 0.242$).

Quenching of Rearrangement of β-Chlorocinnamyl Chloride (9) by 1,3-Cyclohexadiene in Acetonitrile (Direct). β-Chlorocinnamyl chloride (1.14 g, 6.06 mmol) was diluted to 10.0 ml with acetonitrile, and 2.0-ml aliquots of this solution were placed in five preconstricted Pyrex test tubes. To these were added, respectively, 1.0-ml aliquots of 0.06, 0.006, 0.0006, and 0.0 *M* solutions of 1,3-cyclohexadiene in acetonitrile. The samples were then handled as outlined in method B. After irradiation for 150 hr, the following results were obtained: [diene] = 0.0 *M*, 7.8% of **13** ($\phi = 0.018$); [diene] = 0.2 *M*, 9.5% of **13** ($\phi = 0.022$); [diene] = 0.02 *M*, 8.2% of **13** ($\phi = 0.019$); [diene] = 0.002 *M*, 6.5% of **13** ($\phi = 0.015$); [diene] = 0.0002 *M*, 6.4% of **13** ($\phi = 0.015$).

Quenching of Rearrangement of β-Chlorocinnamyl Chloride (9) by 1,3-Cyclohexadiene in Acetone–Acetonitrile. β-Chlorocinnamyl chloride (2.83 g, 14.0 mmol) was diluted to 20.0 ml with acetone–acetonitrile solution, and 2.0-ml aliquots of this were placed in seven preconstricted Pyrex test tubes. To these were added, respectively, 1.0-ml aliquots of 3.0, 0.3, 0.03, 0.003, 0.0003, 3×10^{-5}, and 0.0 *M* solution of 1,3-cyclohexadiene in acetone–acetonitrile. The samples were then handled as outlined in method B. After irradiation for 28.3 hr and work-up as described before, the following results were obtained: [diene] = 0.0 *M*; 16.4% of **13** ($\phi = 0.25$); [diene] = 1.0 *M*, 1.1% of **13** ($\phi = 0.017$); [diene] = 0.1 *M*, 1.0% of **13** ($\phi = 0.015$); [diene] = 0.01 *M*, 3.1% of **13** ($\phi = 0.046$); [diene] = 0.001 *M*, 10.0% of **13** ($\phi = 0.154$); [diene] = 0.0001 *M*, 15.6% of **13** ($\phi = 0.229$); [diene] = 10^{-5} *M*, 16.0% of **13** ($\phi = 0.244$).

Quenching of Rearrangement of β-Phenylcinnamyl Chloride (10) with 1,3-Cyclohexadiene in Acetone–Acetonitrile. β-Phenylcinnamyl chloride (0.740 g, 3.24 mmol) was diluted to 10.0 ml with acetone–acetonitrile solution, and 2.0-ml aliquots of this were placed in five preconstricted Pyrex test tubes. To these were added, respectively, 1.0-ml aliquots of 3.0, 0.3, 0.2, 0.1, and 0.0 *M* 1,3-cyclohexadiene in acetone–acetonitrile. The samples were then handled as outlined in method B. After irradiation for 50 hr and work-up as previously described, the following results were obtained: [diene] = 0.0 *M*, 17.6% of **15** ($\phi = 0.086$); [diene] = 1.0 *M*, 6.1% of **15** ($\phi = 0.026$); [diene] = 0.1 *M*, 5.9% of **15** ($\phi = 0.025$); [diene] = 0.067 *M*, 7.5% of **15** ($\phi = 0.033$); [diene] = 0.033 *M*, 10.1% of **15** ($\phi = 0.046$).

Quantum Yield Determination of β-Phenylcrotyl Chloride (12) in Acetone–Acetonitrile. β-Phenylcrotyl chloride (0.343 g, 2.06 mmol) was diluted to 10.0 ml in acetone–acetonitrile solution and 3.0 ml-aliquots were placed in two preconstricted Pyrex test tubes. The samples were then handled as outlined in method B. After 36 hr of irradiation and work-up as described before, one of the tubes contained 8.4% of **18** ($\phi = 0.046$), while the other contained 7.1% of **18** ($\phi = 0.039$).

Quenching of Rearrangement of β-Phenylcrotyl Chloride (12) by 1,3-Cyclohexadiene in Acetone–Acetonitrile. β-Phenylcrotyl chloride (0.217 g, 1.63 mmol) was diluted to 10.0 ml with acetone–acetonitrile solution, and 2.0-ml aliquots of this were placed in four preconstricted Pyrex test tubes. To these were added, respectively, 1.0-ml aliquots of 0.18, 0.09, 0.03, and 0.0 *M* solutions of 1,3-cyclohexadiene in acetone–acetonitrile. The tubes were handled as outlined in method B, and after 36 hr of irradiation and work-up as before, the following results were obtained: [diene] = 0.0 *M*, 8.2% of **18** ($\phi = 0.045$); [diene] = 0.01 *M*, 6.9% of **18** ($\phi = 0.038$); [diene] = 0.03 *M*, 1.8% of **18** ($\phi = 0.009$); [diene] = 0.06 *M*, 0.9% of **18** ($\phi = 0.004$).

Quantum Yield Determination of β-Chlorocrotyl Chloride (11) in Acetone–acetonitrile. β-Chlorocrotyl chloride (0.299 g, 2.39 mmol) was diluted to 10.0 ml with acetone–acetonitrile solution, and 3.0-ml aliquots of this were placed in two preconstricted Pyrex test tubes. The samples were then handled as described in method B. After 19 hr of irradiation and work-up as described before, one of the tubes contained 7.2% of **17** ($\phi = 0.076$), while the other contained 6.5% of **17** ($\phi = 0.070$).

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Registry No.—(*E*)-**9**, 53834-49-4; (*Z*)-**9**, 53834-50-7; (*E*)-**10**, 53834-51-8; (*Z*)-**10**, 53834-52-9; (*E*)-**11**, 15224-29-0; (*Z*)-**11**, 26310-41-8; (*E*)-**12**, 53783-48-5; (*Z*)-**12**, 53783-48-5; **13**, 55783-49-6; **14**, 2415-80-7; **15**, 53808-79-0; **17**, 7013-11-8; **18**, 53785-50-9; **19**, 1727-64-6; (*E*)-**21**-Tl, 53783-51-0; (*Z*)-**21**-Tl, 53783-52-1; (*E*)-**21**-Me, 53783-53-2; (*Z*)-**21**-Me, 53783-54-3; **22**-Tl, 55783-55-4; **22**-Me, 53783-56-5; (*E*)-β-phenylcinnamyl alcohol, 22835-64-9; (*E*)-β-chlorocinnamyl alcohol, 53783-57-6; (*E*)-β-chlorocrotyl alcohol, 53783-58-7; β-phenylcrotonaldehyde, 4411-89-6; (*E*)-β-phenylcrotyl alcohol, 53783-59-8; (*Z*)-β-phenylcrotyl alcohol, 53783-60-1; 1,3-cyclohexadiene, 592-57-4.

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Photocatalyzed Reaction of Trifluoromethyl Iodide with Steroidal Dienones[1]

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Ultraviolet irradiation (3500 Å) of pyridine solutions of 3-keto-$\Delta^{4,6}$-steroids in the presence of trifluoromethyl iodide gave 3-keto-4-trifluoromethyl-$\Delta^{4,6}$-steroids as the sole products of reaction. A similar reaction of using 7-oxo-3,5-androstadien-17β-yl acetate gave a mixture of 6-trifluoromethyl-7-oxo-$\Delta^{3,5}$-steroid and 3-trifluoromethyl-7-oxo-Δ^{5}-steroid indicating a steric as well as an electronic requirement for this reaction. An interesting reductive solvolysis of the 4-trifluoromethyl group has been observed.

In the course of preparing trifluoromethylated steroids,[2] we attempted photochemical addition of trifluoromethyl iodide to the 3-keto-$\Delta^{4,6}$ system. Haszeldine has shown the trifluoromethyl group adds selectively to the terminal vinyl carbon when acrylic acid derivatives are exposed to trifluoromethyl iodide under photolytic conditions.[3] The position of addition in these cases was not dependent upon polarization of the double bond but on the stability of the intermediate radical. Accordingly, Godfredsen and Vangedal demonstrated that addition to the steroidal 3-alkoxy-$\Delta^{3,5}$ system resulted in substitution at the 6 position.[4] Wolff found addition to Δ^{3}-5α-steroids gives exclusively the axial 3α-trifluoromethylated product,[5] a result expected if one invoked steric considerations. We find trifluoromethyl substitution occurs preferentially α to the carbonyl function in linearly conjugated dienone systems. Both electronic and steric considerations must then be involved in the addition of the trifluoromethyl radical to these electron-deficient systems.

Irradiation of a solution of dienones **1a–d** in a mixture of pyridine and trifluoromethyl iodide with uv light (3500 Å) for 2–6 days at room temperature gave 4-trifluoromethylated steroids **2a–d** as the only products (32–42% conversion) found in addition to starting material. That the trifluoromethyl group was in the 4 position was evidenced by PMR absorption of vicinal vinyl hydrogens at C-6 and C-7 (complex doublets at about τ 3.7 and 3.3, $J \simeq 11$ Hz). This absorption disappeared when **2a** and **2b** were hydrogenated in ethyl acetate in the presence of palladium–barium sulfate catalyst to give 3-keto-Δ^{4} derivatives **3a** and **3b**. It is interesting that compounds **2** and **3**, with maxima at 283 and 233 nm, respectively, show no bathochromic shift on substitution of a trifluoromethyl group for a hydrogen α to the carbonyl.

The "reversed" linear dienone **4** when irradiated in the presence of trifluoromethyl iodide led to two products in addition to recovered starting material. The major product isolated was 6-trifluoromethyl-3,5-dien-7-one (**5**) formed in