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A Unique Reversal of Regioselectivity in
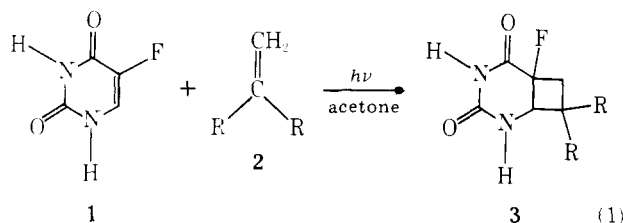# the Photoaddition of 2-Fluorocyclohexenone to Isobutylene

Mark L. Greenlee,[1a] Edward L. Fritzen, Jr., and John S. Swenton*[1b,c]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210
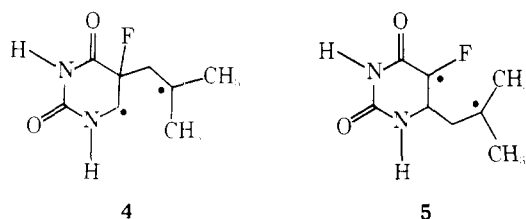
The preparation of 2-fluorocyclohex-2-enone (13) via the chlorofluorocarbene adduct of the morpholine enamine of cyclopentanone is described. The photocycloaddition reactions of 13 and isobutylene have been studied. In contrast to the highly regioselective additions of its pyrimidinone analogue (5-fluorouracil), 13 exhibits products from predominantly the head-to-head orientation. The mechanistic implications of these results are briefly discussed.

While photochemical cycloaddition reactions of α,β-unsaturated carbonyl compounds have been extensively utilized in organic synthesis,[2] the low regioselectivity of the reaction with simple olefins detracts from the synthetic method.[2d,3] We recently reported that substitution of the 5 hydrogen of uracil for fluorine remarkably enhances the regioselectivity of the photoaddition reaction with simple olefins[4] (eq 1). Since


the photoaddition reactions of uracil and cyclohexenone to isobutylene afford similar regioselectivity,[5] the photoadditions of 2-fluorocyclohex-2-enone (13) to olefins were of interest as a potential method of regiospecific four-ring annulation.

A second impetus for a study of the photochemistry of 13 relates to a possible origin for the highly regioselective addi-

tions of fluorouracil. Thus, in the fluorouracil system this high selectivity could be rationalized if biradical 4 had had an enhanced efficiency of ring closure relative to biradical 5.[6] This possibility was made especially attractive by the work of Wagner and Thomas,[9] who showed that the ratio of fragmentation to closure in the biradical derived from butyrophenone was markedly altered by substitution of fluorine for
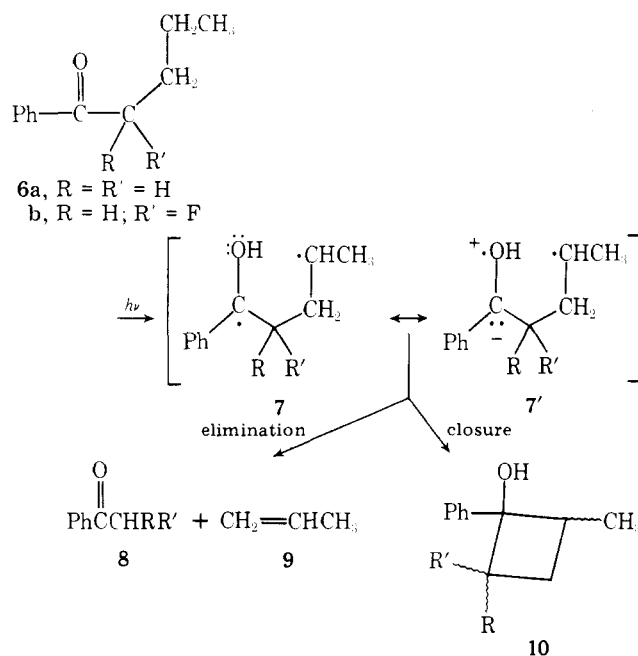
hydrogen. For **6a** Φ_{cyc}/Φ_{elim} was 0.23, while the value for **6b** was >60. These workers proposed that hyperconjugative interaction (i.e., **7′**) introduced a conformational bias in the biradical favoring closure. A critical requirement for such an effect is a heteroatom possessing a lone pair of electrons adjacent to the radical center. Since biradical **4** formally has this required structural feature but a biradical derived from photoaddition of **13** to olefins would not, the photochemistry of **13** could aid in establishing the importance of the heteroatom on cycloaddition regioselectivity.

We report here that **13** undergoes photochemical reaction with isobutylene to afford products of reversed regioselectivity relative to that of cyclohexenone. Thus, the high head-to-tail orientation observed for 5-fluorouracil photoadditions is not carried over to 2-fluorocyclohexenone.
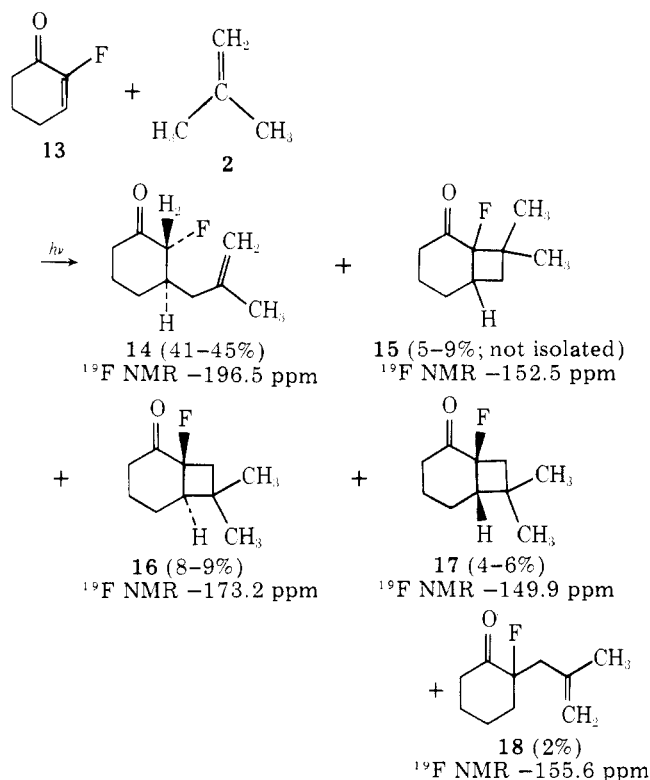
Synthesis of 2-Fluorocyclohex-2-enone (13). When this work was initiated, we were not aware of general routes to α-fluorocyclohexenones;[10] thus, our synthesis of **13** followed the ring expansion route for the related α-chlorocyclohexenone.[11] Reaction of chlorofluorocarbene with the morpholine enamine of cyclopentanone followed by hydrolysis afforded **13**. While this route would be expected to produce the two isomeric bicyclic intermediates **12a** and **12b**, which via con-

12a, X = Cl; X′ = F
 b, X = F; X′ = Cl
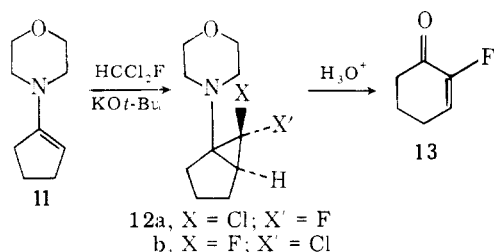
certed ring opening would afford a mixture of 2-chloro- and 2-fluorocyclohexenone, only the latter was isolated. Plausibly this could be due to the preferential solvolysis of the chlorine under the mild hydrolysis conditions employed here.[12] While the overall yield for the sequence is a modest 22%, the ready availability of the starting materials allowed convenient preparation of gram amounts of **13**. The enone exhibited the expected ^{19}F resonance at −132.96 ppm (d, $J = 14$ Hz), a doublet of triplets at τ 3.59 ($J = 14$ and 4 Hz) for H$_3$, strong IR absorptions at 1701 and 1653 cm^{-1}, and a typical cyclohexenone ultraviolet spectrum, λ_{max} (hexane) 228 nm (ϵ 25 000) and 322 (36).

Photoaddition of 2-Fluorocyclohexenone to Isobutylene. To facilitate comparison of the results of this work with the earlier studies on cyclohexenone, irradiation conditions were similar to those employed in the earlier study.[2a] Thus, irradiation of **13** with an excess of isobutylene in pentane at 0 °C with Pyrex-filtered light from a 450-W Hanovia medium-pressure source gave six products in ratios independent of conversion of **13**, as deduced from the ^{19}F spectrum of the crude reaction mixture. The ^{19}F spectrum also furnished preliminary evidence on structure since secondary fluorines α to ketones in five- to seven-membered cyclic ketones show ^{19}F resonance at −194 to −186 ppm[13] and tertiary fluorines show absorption in the range −159 to −154 ppm.[13] Thus, the major product (i.e., **14**) appeared to have fluorine on a secondary position, while three products (**15**, **17**, and **18**) were tertiary fluorides and a third (**16**) had a somewhat anomalous resonance.

The structural assignment for the major product as **14** was fully established by spectroscopic and chemical means. The ^{1}H NMR spectrum showed an allylic methyl group at τ 8.23, two vinyl protons, and H$_2$ as a partially obscured doublet of doublets ($J_{H_2,F} = 48$ Hz, $J_{H_2,H_3} = 9$ Hz) which collapses to a clean doublet when the fluorine is decoupled. The ^{19}F NMR spectrum appears as a doublet of doublets[14] ($J = 48$ and ~5

13 + 2

14 (41–45%)
^{19}F NMR −196.5 ppm

15 (5–9%; not isolated)
^{19}F NMR −152.5 ppm

16 (8–9%)
^{19}F NMR −173.2 ppm

17 (4–6%)
^{19}F NMR −149.9 ppm

18 (2%)
^{19}F NMR −155.6 ppm

Hz). The position and HF coupling are in agreement with those expected for a cyclic α-fluoro ketone[13a] (α-fluorocyclohexanone, −186 ppm, $J = 49$ Hz). The trans stereochemistry was assigned on the basis of the magnitude of the vicinal coupling constants ($J_{H_2,H_3} = 9$ Hz, $J_{H_3,F} = ~5$ Hz), which agree with those expected for the trans but not the cis stereochemistry (Chart I). Reduction of **14** with lithium and ammonia followed by Jones oxidation afforded the known **19**.

The product second in abundance has been assigned **16**. Its ^{1}H NMR spectrum shows saturated methyl groups at τ 8.85 (s) and 8.67 (d, $J = 1.5$ Hz). The doublet methyl group collapses to a singlet when the fluorine is decoupled. The ^{19}F NMR spectrum shows a broad structured singlet of width at half-height of 60 Hz, consistent with fluorine being coupled to three nonequivalent adjacent hydrogens as well as to one of the methyl groups. The assignment of the trans stereochemistry at the ring juncture derives from the coupling of the fluorine to one of the methyl groups. Models indicate that the requirement of the intersection of vectors along the C–H and C–F bonds for long range fluorine–hydrogen coupling (Converging Vector Rule)[17,18] is nicely accommodated by the trans-fused isomers. We have never observed such coupling in the fluorouracil adducts which are all cis.[4] Furthermore, the somewhat abnormal position of the fluorine resonance may be associated with the trans-fused ring system.

The cis-fused head-to-tail cycloadduct, **17**, comprises 4–6%

Chart I. Expected Vicinal Coupling Constants in the Preferred Conformation of 14 and Its Cis Isomer

system	dihedral angle, deg	expected J, Hz	system	dihedral angle, deg	expected J, Hz
H$_2$–H$_3$	180	~12–13[15]	H$_2$–H$_3$	60	~3[16]
H$_3$–F	60	<5[16,17]	H$_3$–F	180	>15[16]

Table I. Product Proportions Obtained from the Irradiation of Cyclohexenone and 2-Fluorocyclohexenone with Isobutylene

R = H	43	11	23	13	10
R = F	12–13	6–9	3	59–65	8–13

14 → 19
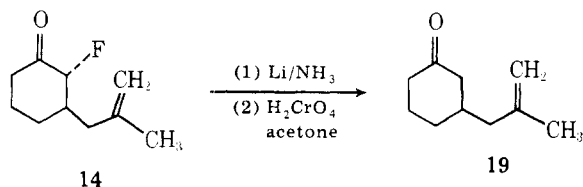
of the reaction mixture and shows saturated methyl groups at τ 8.72 and 9.01 in its ^{1}H NMR spectrum. The ^{19}F NMR spectrum of 17 shows a five-line multiplet similar to spectra observed in the cycloadducts of fluorouracil and disubstituted olefins.[4] The product assigned as 18 was very minor (2%). Its ^{1}H NMR spectrum showed an allylic methyl group at τ 8.22 and two protons as a multiplet at τ 5.08–5.24, while its ^{19}F NMR spectrum exhibited a broad multiplet from −156.2 to −155.1 ppm.

Two products observed in the ^{19}F NMR spectrum have not been isolated despite extensive efforts. One of these formed in 5–9% yield shows a clean doublet ($J = 22$ Hz) in the ^{19}F NMR spectrum at −152.5 ppm. This is the position expected for cycloadduct 15, which would contain a tertiary fluorine and which should show a coupling constant of about 20 Hz for the HF dihedral angle close to 0°.[14] The product appearing as a doublet ($J = 46.8$ Hz) at −187.4 ppm disappeared on passage of the product mixture through a silica gel column and was not characterized.

Discussion

The results presented here show that in contrast to 5-fluorouracil, 2-fluorocyclohexenone shows no tendency to give a highly regioselective head-to-tail photocycloaddition to isobutylene. In fact, the ca. 1:3 (head-to-head/head-to-tail) product ratio observed here is opposite to the 3:1 regioselectivity observed for the parent cyclohexenone–isobutylene system (Table I). Since uracil and cyclohexenone show similar regioselectivity in photoadditions to isobutylene, both the heteroatom at the 4 position and the fluorine must play a role in the highly selective photocycloadditions observed for 5-fluorouracil.

A second point in the work is the effect of fluorine in increasing the amount of the disproportionation product in the reaction. This may relate to Meinwald's comments concerning the preference for two tertiary radicals to disproportionate rather than couple.[19] The high preference for formation of the trans compound 14 is explainable on the basis of stereoelectronic consideration for hydrogen transfer at the biradical stage. Thus, models indicate that a *cis*-decalin type transition state allows the hydrogen being transferred and the adjacent half-filled p orbital to be nearly coplanar.[20,21] This ideal stereoelectronic situation cannot be obtained in a *trans*-decalin transition state.
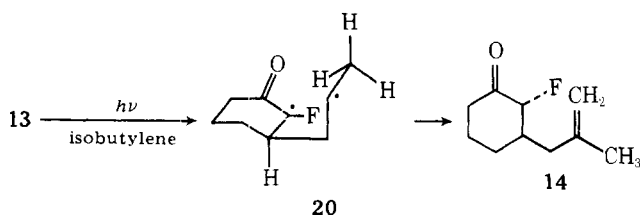
One of our goals in initiating this work was to develop a procedure for controlling the regioselectivity of cycloadduct formation in reactions of cycloalkenones with simple olefins. Unfortunately, fluorine substitution in this system not only gives poor regioselectivity in the additions but results primarily in the formation of disproportion-type products. Obviously, an alternate approach to solving this general problem must be employed.

2-Fluorocyclohex-2-enone (13). A mixture of 13.0 g (0.085 mol) of 1-morpholino-1-cyclopentene and 19.0 g (0.17 mol) of freshly sublimed potassium *tert*-butoxide in 300 mL of anhydrous tetrahydrofuran was cooled to −45 °C. To this stirred suspension, under nitrogen, was added 15 mL (21 g, 0.2 mol) of dichlorofluoromethane in 85 mL of tetrahydrofuran dropwise over 6 h. The resulting orange suspension was stirred for an additional 1 h while it warmed to room temperature, and then 300 mL of solvent was distilled off at 30–40 °C (150 mm). The residual orange-brown paste was dissolved in 100 mL of a 5% aqueous hydrochloric acid solution and stirred for 1 h at room temperature. The small organic layer was separated, and the aqueous layer was extracted with ethyl ether (3 × 50 mL). The organic phases were combined, washed successively with a 5% aqueous sodium bicarbonate solution (2 × 25 mL), water (25 mL), and a saturated sodium chloride solution (25 mL), and dried over anhydrous calcium sulfate. Filtration and removal of the solvent in vacuo (25 °C, 25 mm) left 16 g of a brown oil. Column chromatography on silica gel (5% ether in petroleum ether eluent) followed by molecular distillation (60 °C, 10 mm) gave 2.17 g (22%) of 13 as a clear oil: IR (CCl$_4$) 1701 (C=O), 1653 (C=C) cm^{-1}; UV λ$_{max}$ (hexane) 228 nm (ε 26 000), 322 (36); ^{1}H NMR δ 1.9–2.7 (6 H, m), 6.41 (1 H, d of t, $J = 14$ and 4 Hz); ^{19}F NMR −132.96 ppm (d, $J = 14$ Hz). Exact mass: calcd for C$_6$H$_7$FO, 114.0481; found, 114.0483.

Photoaddition of 2-Fluorocyclohexenone to Isobutylene. All irradiations were performed with a Hanovia immersion well using Pyrex-filtered light from a Hanovia Type I 450-W medium-pressure source. The reactor was charged with a solution of 237 mg (2.1 mmol) of 2-fluorocyclohexenone in 150 mL of purified pentane. Dry nitrogen was bubbled through the solution for 1 h, the reactor was cooled, and isobutylene was bubbled into the solution through the nitrogen inlet until the volume had increased by 20 mL (>100 equiv). The inlet was then replaced with a serum cap, and the stirred solution was irradiated. The progress of the reaction was followed by analyzing aliquots by VPC (column A, 150 °C, nitrogen flow 30 mL/min). The reaction was essentially complete after 6 h, and the pentane and isobutylene were removed in vacuo. An ^{19}F NMR spectrum of the residual yellow oil showed the presence of six fluorine-containing products, and integration of the spectrum gave the percentage of the reaction mixture that each comprised: 17, −149.9 ppm (m), 6–9%; 15, −152.52 ppm (d, $J = 22$ Hz), 8–13%; 18, −156.2 to −155.1 ppm (m), 1–3%; 16, −173.9 to −172.6 ppm (m), 12–13%; unknown, −187.8 ppm (d, $J = 43$ Hz), 3–6%; 14, −196.51 ppm (d, $J = 47$ Hz), 59–65%. Analytical gas chromatography of the reaction mixture (column B, 100 °C, nitrogen flow 25 mL/min) resolved five components: 16, 5.3 min; 17, 6.8 min; 18, 10.5 min; 15, 18 min; 14, 23.3 min. The reaction mixture was subjected to low-pressure chromatography on a 3 × 95 cm silica gel column; elution was with a 3% solution of ether in petroleum ether and 25-mL fractions were collected. The following results were observed: fractions 63–75, 16; fractions 77–80, 18; and fractions 85–91, 17. After 100 fractions had been collected, the eluent was changed to 25% ether in petroleum ether, and component 14 appeared in fractions 153–164. Component 15 was not observed in any of the fractions. The concentrated fractions were further purified by preparative VPC (column C, 120 °C, helium flow 60 mL/min).

16: IR (CCl$_4$) 2938 (s), 2859 (m), 1728 (s), 1186 (m), 1076 (m), 916 (m) cm^{-1}; ^{1}H NMR (60 MHz) τ 7.1–8.6 (struc. envelope, 9 H), 8.5 (s, 3 H), 8.67 (d, $J = 1.5$ Hz, 3 H). Fluorine decoupling collapses the τ 8.67

doublet into a sharp singlet as well as markedly simplifying the τ 7.1–8.6 region; ^{19}F NMR −172.6 to −173.9 ppm (br mult). Exact mass: calcd for $C_{10}H_{15}FO$, 170.1107; found, 170.1109.

17: IR (CCl_4) 2937 (s), 2853 (m), 1727 (s), 1457 (m), 1373 (m), 1217 (m), 1138 (m), 1028 (m), 997 (m) cm^{-1}; ^{1}H NMR τ 7.18–7.73 (struc. mult), 7.82 (br s), 7.90–8.58 (struc. mult) (integrating for a total of 9 H), 8.72 (s, 3 H), 9.01 (s, 3 H); ^{19}F NMR −149.48, −149.67, −149.75, −149.94, −150.03, −150.23 ppm. Exact mass: calcd for $C_{10}H_{15}FO$, 170.1107; found, 170.1109.

18: ^{1}H NMR (60 MHz) τ 4.76 (struc. s, 1 H), 4.91 (struc. s, 1 H), 7.27–7.90 (struc. mult, 4 H), 7.9–8.5 (partially obscured mult, 6 H), 8.22 (br s, 3H); ^{19}F NMR −156.2 to −155.1 ppm (br mult).

14. The material isolated from the column was recrystallized from petroleum ether to give white crystals: mp 43–45 °C; IR (CCl_4) 2929 (br mult), 1740 (s), 1100 (m), 902 (m) cm^{-1}; ^{1}H NMR (60 Hz) τ 5.18 and 5.26 (br s, 2 H), 5.48 (d of d, J = 48 and 10 Hz, 1 H), 7.36–7.78 (br mult, 3 H), 7.78–8.30 (br mult, 3 H), 8.28 (br s, 3 H), 8.28–8.90 (br mult, 3 H). Fluorine decoupling collapsed the doublet of doublets centered at τ 5.48 to a clean doublet (J = 10 Hz); ^{19}F NMR −196.51 ppm (d, J = 47 Hz); there was further undefined coupling <6 Hz. Exact mass: calcd for $C_{10}H_{15}FO$, 170.1107; found, 170.1109.

In a reaction similar to that described above, 1.109 g (9.73 mmol) of 13 in 120 mL of pentane and 50 mL of isobutylene was irradiated at 0 °C for 15 h. Solvent removal in vacuo yielded 1.86 g of colorless liquid which was filtered through silica gel (25% ether–hexane) and molecularly distilled (45–50 °C, 10 mm) to afford 1.07 g (65%) of photoadduct mixture.

Reduction of 14 to 19. A 45-mg (0.27 mmol) portion of 14 was dissolved in 15 mL of anhydrous liquid ammonia at −33 °C in a 25-mL three-neck flask equipped with a dry ice condenser and a magnetic stirring bar. To the stirred solution was added lithium wire in approximately 4-mg (0.58 mmol) portions until the resulting blue color persisted for 30 min (2 portions, >4 equiv). The solution was stirred for an additional 1 h, and then the ammonia was allowed to evaporate. The remaining white salts were dissolved in 5 mL of an aqueous ammonium chloride solution, and the solution was extracted with ether (3 × 5 mL). The extracts were combined, washed with water (2 mL), and concentrated by rotary evaporation. The yellow residue was dissolved in 2 mL of acetone, and the solution was transferred to a 10-mL two-neck flask equipped with a magnetic stirring bar. To the stirred solution was added Jones reagent via a syringe until the orange color persisted for 30 min (~50 μL). The mixture was filtered into another 10-mL flask and the green salts were rinsed with 1 mL of acetone. Isopropyl alcohol was added dropwise to the solution until the excess oxidant was consumed (indicated by a green color). The solution was then stirred for 1 h with 100 mg of sodium bicarbonate, filtered, and concentrated in vacuo, leaving a yellow oil. VPC analysis (column B, 110 °C, nitrogen flow 25 mL/min) indicated the presence of two components in about a 2:1 ratio, the minor appearing to be unreduced 14 based on its retention time. The two components were separated by preparative VPC (column D, 120 °C, helium flow 40 mL/min), yielding 3.5 mg of recovered 14 and 5 mg (13%) of a clear oil which exhibited the spectral characteristics (IR and NMR) reported for 19.[2a]

Supplementary Material Available: ^{1}H and ^{19}F NMR spectra and decoupling results (9 pages). Ordering information is given on any current masthead page.

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(21) A. L. J. Beckwith and C. Easton, *J. Am. Chem. Soc.*, **100**, 2913 (1978).
(22) Melting points were obtained in open capillaries using a Thomas-Hoover "Unimelt" apparatus and are uncorrected. Infrared spectra were measured in carbon tetrachloride on a Perkin-Elmer Model 467 spectrophotometer. ^{1}H NMR spectra were obtained in deuteriochloroform on a Varian Associates A60-A or a Bruker Hx-90 nuclear magnetic resonance spectrometer using tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts are reported in τ (parts per million shift downfield from Me_4Si). ^{19}F NMR spectra were obtained in deuteriochloroform on a Bruker Hx-90 MHz instrument. The NMR chemical shifts are reported in parts per million relative to $CFCl_3$ by subtracting 162.9 ppm from the shift observed from hexafluorobenzene. Ultraviolet spectra were measured in a Cary 15 ultraviolet spectrophotometer. Mass spectral measurements were obtained in a MS-9 double-focusing mass spectrometer. Analyses by VPC were made using a Varian Aerograph Series 1200 gas chromatograph fitted with column A ($^1/_8$ in. × 14 ft, 5% SE-30 on 60–80 mesh Chromosorb G) or column B ($^1/_8$ in. × 5 ft, 3% SF-96 on 60–80 mesh Chromosorb G). Preparative VPC work was carried out using a Varian Model 700 Autoprep fitted with column C (0.25 in. × 6 ft, 5% SE-30 on 60–80 mesh Chromosorb G).