(coupling constant about 0.4 G) centered at about −48 ppm relative to CF_3COOH. The line widths of the peaks (0.1–0.15 G) seem to indicate the presence of fluorine in intercalated molecules capable of translatory motion, but additional inferences about the structure are unwarranted at present.

A thermogravimetric analysis of the intercalate was carried out on a Mettler thermoanalyzer. The compound begins to lose weight slowly around 80°, but rapid weight loss occurs only at 450° and appears to be complete at 575°. Appreciable quantities of CF_4 (24%) and C_2F_6 (12%) were observed in addition to xenon (64%) in a mass spectrometric analysis of the gases collected under vacuum in a separate experiment. Not all the xenon in the original sample was recovered. It was possibly retained in the graphite in the form of an extremely stable "residue compound". The x-ray pattern of the residue gave a very intense peak at 3.48 Å, indicative of graphite with a slightly expanded lattice. No xenon fluorides were liberated upon heating. It is thus difficult to ascertain whether "$C_{19}XeF_6$" is a true intercalation compound in the same sense as $C_{8.7}IF_5$ which again liberates IF_5 upon heating above 80°.[1,3] On the other hand, the intercalate $C_{10}AsF_5$ has been found to liberate both AsF_5 and AsF_3 upon heating, the latter particularly at higher temperatures.[10] It can therefore be expected that a strong fluorinating agent such as XeF_6 would fluorinate graphite at higher temperatures to yield carbon fluorides.

After removal of excess XeF_6, the intercalate can be easily handled outside the vacuum line and gives off HF only very slowly. Presumably, the intercalated XeF_6 is eventually hydrolyzed to the explosive XeO_3. Upon standing at room temperature in the open for 1 week, the material neither showed noticeable change nor was shock sensitive. A certain amount of caution is advised, however, in handling the material. This ease of handling may lend it useful and facile fluorination properties in organic chemistry. Indeed, treatment of phenanthrene in dichloromethane solution with 1 mole equiv of the XeF_6–graphite intercalate at 0–25 °C under anhydrous conditions in an open system, yielded fluorine substitution and addition products. The ^{19}F NMR spectrum of the crude reaction mixture (after aqueous sodium bicarbonate work-up) contained the following signals:[11] δ 194.6 (relative area 13), 152.8 (3), 125.2 (55), 122.4 (6), 118.8 (3), 115.6 (7), 113.3 (3), 110.3 (6), and 107.9 (3). Careful column chromatography on silica gel, petroleum ether (40–60°) serving as eluent, afforded 9-fluorophenanthrene as colorless needles, mp 51–53°, in 34% yield. It was identified by melting point (lit.[12] 51–52°), elemental analysis, mass spectrum, and the ^{19}F NMR spectrum[11] (δ 125.2, doublet of doublets (dd), J_1 = 11.9 Hz, J_2 = 2.0 Hz; lit.[13,14] δ 125.3, dd, J_1 = 11.8 Hz; J_2 = 2.0 Hz).

The ^{19}F NMR signal at 194.6 (doublet of triplets, J_1 = 50.1 Hz, J_2 = 15.6 Hz) is indicative of a fluorine addition product, possibly 9,9,10-trifluoro-9,10-dihydrophenanthrene. This tentative suggestion is consistent with the prominent signal at *m/e* 234 ($C_{14}H_9F_3^+$) in the mass spectrum of the crude reaction mixture.[15] On the basis of the results outlined above, the xenon hexafluoride–graphite intercalate may become a useful mild fluorinating agent of aromatic systems.

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Henry Selig,* Mordecai Rabinovitz
Israel Agranat, Chun-Hsu Lin
Institute of Chemistry, Hebrew University
Jerusalem, Israel

Lawrence Ebert
Exxon Corporation
Linden, New Jersey 07036

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Fluorine Control of Regioselectivity in Photocycloaddition Reactions. The Direct Functionalization of Uracil via a Novel 1,4-Fragmentation

Sir:

While photochemical cycloaddition reactions of α,β-unsaturated systems have been extensively employed in organic synthesis,[1] the lack of regioselectivity in additions of simple olefins[1d,2] detracts from the reaction's general utility. In connection with synthetic studies of nucleic acid bases,[3] we encountered the above problem and wish to report here the powerful influence of a fluoro-substituent in controlling regioselectivity. In addition, a novel 1,4-fragmentation reaction has been uncovered which amplifies the utility of 5-fluorouracil as a photochemical synthon for the 5-uracil carbanion.[3] Extension of these observations to enone photocycloaddition reactions would offer a rational method for controlling regioselectivity in these systems also.

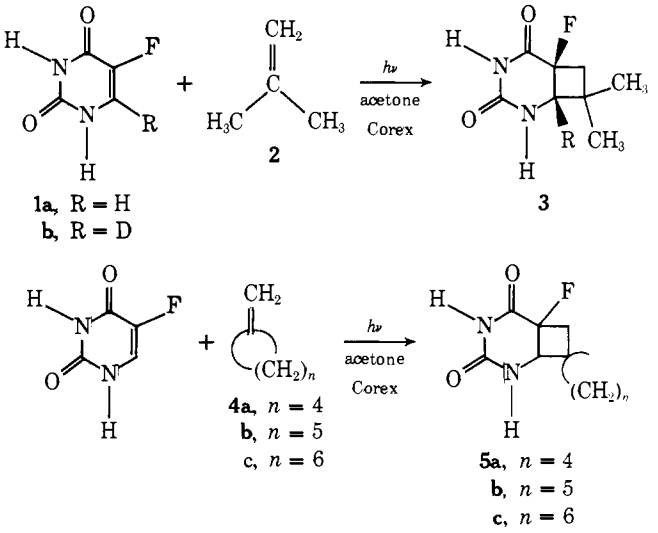
Regarding regioselectivity, uracil, thymine, and 6-methyluracil show unexceptional behavior in their photocycloaddition reactions to isobutylene (Table I). Thus, the steric effect of the vinylic methyl has little influence on regioselectivity, and the modest preference for the 8,8- vs. the 7,7-dimethyl compound (3.4:1) is reminiscent of that noted for the cyclohexenone–isobutylene system (3.3:1).[2a] Strikingly, 5-fluorouracil shows complete regioselectivity in its acetone-sensitized reaction with isobutylene (**2**), methylenecyclopentane (**4a**), methylenecyclohexane (**4b**), and methylenecycloheptane (**4c**). In each case only one product was observed by VPC and TLC. This material could be obtained analytically pure in high yield by simple recrystalli-

Table I. Regioselectivity of Photoadditions[a]

Uracil (mmol)	Olefin (mmol)	Irradiation time, h	% Yield	Cycloadducts (mp, °C) 8-substituted	Cycloadducts (mp, °C) 7-substituted	Ratio (head-to-tail)/ (head-to-head)
Uracil[b] (0.21)	**2** (120)	4.5	92[c]	97-98[e]	liquid[e]	3.4
Thymine[b] (0.60)	**2** (120)	4.5	92[c]	240-241	255-256	3.4
6-Methyluracil[b] (0.95)	**2** (120)	3.0	97[c]	197-198	219-220	2.9
5-Fluorouracil (3.0)	**2** (120)	2.0	90[d]	244-245		>50.0
5-Fluorouracil (3.0)	**4a** (45)	2.0	76[d]	265-266		>50.0
5-Fluorouracil (3.0)	**4b** (45)	2.0	72[d]	263-265		>50.0
5-Fluorouracil (4.0)	**4c** (48)	2.3	78[d]	259-260		>50.0
5-Fluorouracil (4.0)	$(CH_3)_2$=C$(CH_3)_2$ (48)	2.3	79[d]	267-268		
5-Fluorouracil (3.0)	1-Methylcyclopentene (45)	2.0	82[c]	232-234[f]		11.0[h]
5-Fluorouracil (3.0)	$CH_3C(H)$=CH_2[i]	2.0	75[c]	239-241[g]		3.0[h]

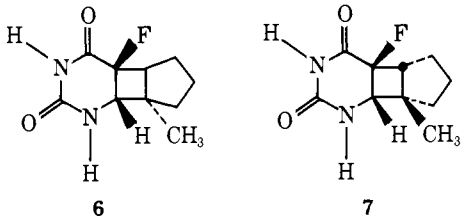
[a] All irradiations were performed in 150 ml of acetone using Corex-filtered light from a 450-W medium-pressure source. [b] The VPC yields and product isolations were performed in acetone:water (7:2) where the uracil has considerably greater solubility. [c] VPC yield of adducts. [d] Yield of recrystallized adduct. [e] These adducts were not separable; thus, they were converted to the 1,3-dimethyl compounds and analyzed as such. [f] The minor adduct has not been isolated pure. [g] This compound is assigned the exo-methyl configuration. [h] Regioselectivity determined by integration of ^{19}F NMR. [i] A saturated solution of propylene was utilized for this irradiation.

Scheme I



zation of the crude reaction mixture. The structures for compounds **3** and **5a-c** were established on the basis of combustion analyses and ^{1}H NMR and ^{19}F NMR spectra.[5]

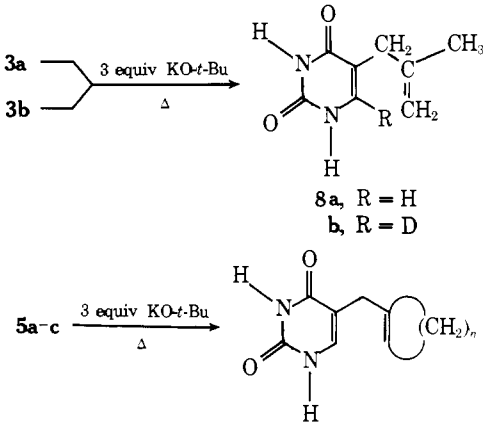
Since propylene shows virtually no preference in its addition to cyclopentenone (ratio of 6- to 7-methyl compound of 1:1.2),[2a] photosensitized addition of **1a** to olefins having more similarly substituted termini was also examined. Photosensitized addition of **1a** to methylcyclopentene followed by integration of the ^{19}F NMR spectrum indicated four cycloadducts to be present in a ratio of 84:7:6:3. The two major components have been assigned structures **6** and **7**,



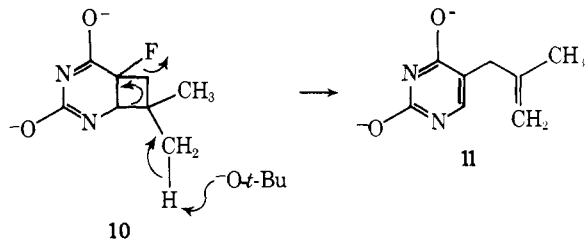
respectively. The reaction thus shows a minimum of 91% regioselectivity. Some loss of specificity was also noted in the reaction of **1a** with propylene. Here four cycloadducts could be detected in a ratio of 45:32:18:5. The two major compounds were assigned as the 8-methyl derivatives and the two minor components as the 7-methyl compounds. Thus, the latter olefins show good, although not complete, regioselectivity in their photoaddition reactions.[6]

Treatment of these adducts with base led to both a novel and synthetically useful reaction (Scheme II). Reaction of

Scheme II

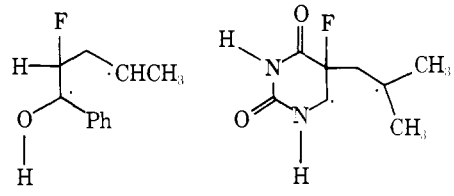


3a with 3 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol at reflux for 0.5 h afforded after work-up **8a** in 83% yield.[7] Similarly, adducts **5a-c** undergo smooth fragmentation under analogous conditions to afford the functionalized bases in yields of 86, 99, and 97%.[8] Mechanisms for this novel fragmentation involving initial 1,2-elimination of hydrogen fluoride followed by reaction of a cyclobutene can be dismissed. The reaction of **3b** (>98% d_1) under these conditions yields **8b** in which no deuterium loss is detectable by NMR. Furthermore, the adduct of **1a** and tetramethylethylene fragments to the respective uracil under conditions similar (a longer reaction time) to those used for **3** and **5a-c.** The mechanism we favor is base-catalyzed reaction of the dianion **10.** While we are unaware of any precedent for such an unactivated hydrogen being involved in a fragmentation process, aromaticity and relief of strain in the product may be important. Especially intriguing is the complete absence of any 1,2-elimination product. The present results extend the utility of 5-fluorouracil as a photochemical synthon for the 5-uracil carbanion. Indeed, with a selective cleavage of the cycloalkene ring, this fragmentation is a method for appending a chain of arbitrary length to the 5-position of the uracil nucleus.



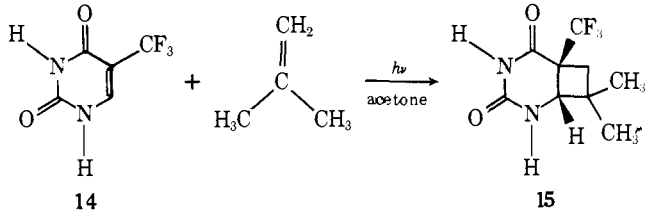
10 11

The origin of the regioselectivity could reasonably result from the effect of fluorine in altering the relative rates of: (1) formation of isomeric exiplexes[1a] or (2) ring closure vs. fragmentation for the 1,4-biradicals produced from collapse of the isomeric exiplexes.[9] Interestingly, Wagner[10] has recently shown that the ratio of ring closure to fragmentation in valerophenone photochemistry is markedly increased by an α-fluorosubstituent and has proposed fluorine hyperconjugation as an important factor in the increased amount of ring closure. The structural similarity of the biradical from α-fluorovalerophenone, **12**, and the presumed biradical intermediate in these cycloadditions, **13**, warrants consider-



12 13

ation of a similar explanation here. While we wish to defer a thorough discussion of this question until completion of mechanistic studies, it is interesting that the acetone photosensitized cycloaddition of 5-trifluoromethyluracil (**14**) to isobutylene affords in 72% isolated yield and with >95% regioselectivity the adduct **15**.[11] Thus, the high electronegativity of the substituent may also play a role in the regioselectivity noted here.



14 15

The photostability of the vinylic fluorine under cycloaddition conditions coupled with the powerful effect of fluorine on regioselectivity and the unique fragmentation processes observed here suggest further utility of fluorinated substrates in organic photochemistry. We are currently studying the cycloaddition reactions of α- and β-fluoro-α,β-unsaturated ketones.[12]

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(4) No ene-products have been observed in any of the reactions of uracils with olefins.

(5) The demanding evidence for the indicated orientation derived from the appearance of H_1 as a simple doublet of doublets due to a large coupling to fluorine (J = 23–24 Hz) and a small coupling to the N–H group (J = ~3 Hz). This latter coupling was completely removed by washing the sample with deuterium oxide.

(6) The observed regioselectivity appears somewhat solvent dependent; a higher regioselectivity has been noted in neat acetone vs. acetone–water mixtures.

(7) For **8**: uv (CH_3OH) 265 nm, ϵ 7200, thymine 265 nm, ϵ 7800; NMR (Me_2SO-d_6 δ 7.13 (s, 1 H, β-uracil hydrogen), 4.67 (br s, 2 H, vinyl), 2.87 (br s, 2 H, methylene), and 2.87 (s, 3 H, methyl).

(8) Mp: **8**, 272–274°; **9a**, 265–267°; **9b**, 277–279°; **9c**, 282–283°.

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(11) **13** had mp 238–239°, NMR (Me_2SO-d_6) 60 MHz δ 1.02 (s, 3 H), 1.08 (s, 3 H), 2.10 (s, 2 H), 3.76 (d, J = 4.5 Hz which collapses to a singlet on addition of D_2O, 1 H), 7.95 (br s, 1 H), and 10.6 (br s, 1 H). The crude ^{19}F NMR of the reaction mixture showed ~ 4–5% of a second fluorine compound which we have not been able to isolate as yet.

(12) All new compounds reported here gave acceptable (±0.3%) C, H, and N combustion analyses.

(13) Camille and Henry Dreyfus Teacher-Scholar, 1970–1975.

Allan Wexler, John S. Swenton* [13]

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received October 29, 1975

Carbon-13 Nuclear Magnetic Resonance Spectra of Zinc(II) Coproporphyrins. A Modus Operandi for Reproducible Measurement of Porphyrin Spectra

Sir:

The use of carbon-13 NMR spectroscopy for the characterization of porphyrins[1] (particularly the identification of type isomers[2]), and in the delineation of the biosynthetic pathway to the type-III porphyrin skeleton[3] is now well established. Insofar as the elegant techniques employed revolve around unambiguous assignment of natural abundance spectra prior to comparison with those of pigments produced enzymically from carbon-13 labeled precursors, it is surprising that only a paucity of systematic work aimed at assignment of porphyrin spectra has been published.[4] We now report a basic method by which reproducible "monomeric" shifts of porphyrin carbons can be simply and easily obtained.

The carbon-13 spectra of virtually all free-base porphyrins show the effects of N–H tautomerism;[5] thus, the α-pyrrole carbons are always broad and unresolved (cf. Figure 1a), and in some cases they are so broad that they escape observation altogether. This exchange process can also effect the β-pyrrole and possibly the meso carbon atoms. Thus, unambiguous assignment of the individual skeletal carbon atoms becomes virtually impossible.

Incorporation of zinc(II) into the porphyrin removes the effects of the tautomeric exchange process. Zinc(II) is diamagnetic and its insertion and removal is a facile undertaking. The resultant carbon-13 NMR spectra give sharp lines for the α (and β) pyrrole carbons (Figure 1b). However, in the course of our study it became clear that the carbon-13 shifts were dependent upon the precise operating conditions (e.g., concentration, temperature, etc.). Moreover, the nature of the fine structure changed markedly with concentration. We ascribe this to the formation of highly structured aggregates in solution.[6]

Despite the generally held view that carbon-13 shifts are not concentration dependent, we have observed shifts of several parts per million in the zinc(II) porphyrins.[7] The carbon-13 shifts of the quaternary skeletal carbons of various porphyrins, even at the same concentration in $CDCl_3$, are quite inconsistent and inexplicable in terms of substituent effects. In retrospect this is not surprising since the observed shifts are a function not only of the isolated molecule