$$C_2H_6 \longrightarrow \quad \overset{H}{\underset{H}{\diagdown}} C{=}C \overset{H}{\underset{H}{\diagup}} \quad + H_2$$

$$\Delta H = \Delta H_f(C_2H_4) - \Delta H_f(C_2H_6) = 33 \text{ kcal}$$

$$C_2H_6 \longrightarrow \quad \overset{H}{\underset{H}{\diagdown}} \overset{\cdot}{C}{-}\overset{\cdot}{C} \overset{H}{\underset{H}{\diagup}} \quad + H_2$$

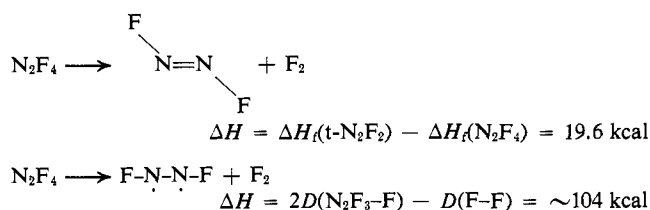$$\Delta H = 2D(C_2H_5{-}H) - D(H{-}H) = 93 \text{ kcal}$$

In nitrogen the energy required to decouple the π-bond overlap is even higher. Computation similar to the above yields approximately 84 kcal.[7,14]

$$N_2F_4 \longrightarrow \quad \overset{F}{\underset{}{\diagdown}} N{=}N \overset{}{\underset{F}{\diagup}} \quad + F_2$$

$$\Delta H = \Delta H_f(t{-}N_2F_2) - \Delta H_f(N_2F_4) = 19.6 \text{ kcal}$$

$$N_2F_4 \longrightarrow F{-}N{-}N{-}F + F_2$$

$$\Delta H = 2D(N_2F_3{-}F) - D(F{-}F) = {\sim}104 \text{ kcal}$$

The experimental 32-kcal activation energy for the isomerization of difluorodiazine is far too low when compared to the rotational barrier of 84 kcal. The nitrogen–nitrogen bond in the transition state has essentially a double-bond character.

The only transition state which might lead to isomerization from the ground state is that having a *linear configuration*, which may not require the high energy needed to overcome a rotational barrier. A transition state of this kind is impossible in the $>C{=}C<$ system.

Acknowledgment. The authors wish to thank Professor S. H. Bauer of Cornell University for very valuable correspondence on this matter.

(14) A. V. Pankratov, *Russ. Chem. Rev.*, **32**, 157 (1963).

(15) In partial fulfillment of the requirements for a Ph.D. thesis to be submitted to the Senate of the Hebrew University by J. B.

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Photoinduced Substitution. IV. Reaction of Aromatic Nitro Compounds with Hydrochloric Acid[1,2]

Sir:

Aromatic nitro compounds are found to react in a relatively clean fashion with concentrated hydrochloric acid when irradiated with ultraviolet light >290 mμ. The major reaction in each case involves reduction of the nitro group to an amino group and replacement of three aromatic hydrogen atoms by chlorine.

The light source used in these studies was a 1200-w G.E. photochemical lamp;[3] radiation below 290 mμ was excluded by a Pyrex filter. Each photoproduct reported was characterized by a mixture melting point with an authentic sample and by the coincidence of the infrared spectrum with that of the known compound.

(1) Part III: R. L. Letsinger and J. H. McCain, *J. Am. Chem. Soc.*, **88**, 2884 (1966).

(2) This work was supported by a Public Health Service Fellowship (1-Fl-GM-29, 771-01 awarded to G. G. W.) and by a National Science Foundation Grant (GP-5715).

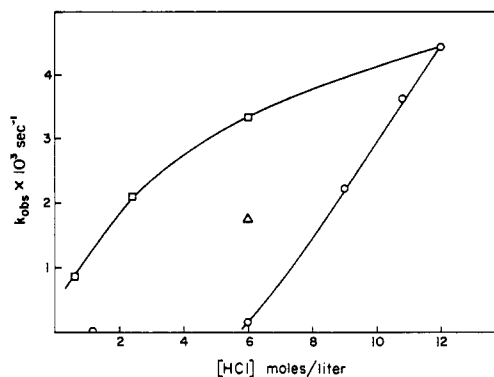(3) R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Am. Chem. Soc.*, **87**, 2945 (1965).

Figure 1. Photoreaction of nitrobenzene in hydrochloric acid: —O—, no added salt; —□—, sufficient LiCl added to give a total chloride concentration of 12 M; —△—, 3 M LiCl present.

When a 2.5×10^{-4} M solution of p-nitrophenol in concentrated hydrochloric acid was irradiated for 1 hr at room temperature in a cuvette, λ_{max} shifted from 320 mμ (A 2.02) to 290 mμ (A 0.74); very little change occurred on further irradiation. For characterization of the products, a solution of 348 mg of p-nitrophenol in 250 ml of concentrated hydrochloric acid in a 500-ml Pyrex flask was flushed with nitrogen and irradiated for 93 hr, at which time the reaction was complete as indicated by the spectrum of a diluted aliquot. Neutralization of the acid, extraction with benzene, and chromatography of a portion (83%) of the extracted products on silica gel yielded 315 mg (71%) of 2,3,6-trichloro-4-aminophenol, mp 170.5–171°, and 84 mg (16%) of tetrachlorohydroquinone, mp 230–232°. Similarly, m-nitrophenol gave 2,4,6-trichloro-3-aminophenol (37%) and 4,6-dichloro-3-aminophenol (24%) as the principal products.
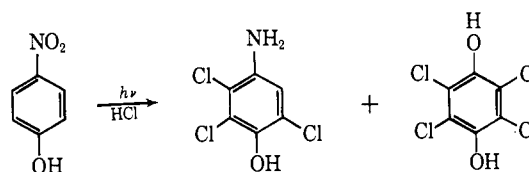
Nitrobenzene reacted somewhat faster than the nitrophenols; the reaction was essentially complete (λ_{max} 273 mμ (A 1.38) $\rightarrow \lambda_{max}$ 288 mμ (A 0.28)) within 25 min when a 2×10^{-4} M solution of nitrobenzene in concentrated hydrochloric acid was irradiated in a cuvette. In preparative experiments 2,4,6-trichloroaniline (44–62% yields) and 2,4-dichloroaniline ($\sim$10%) were obtained from mixtures of nitrobenzene (308 mg) in 500 ml of concentrated hydrochloric acid irradiated for 10 hr.
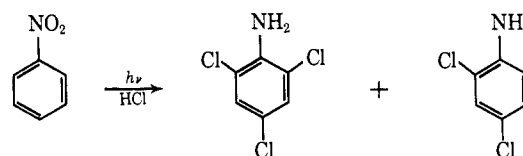
Rate data for the decrease in absorbance at 273 mμ for solutions of nitrobenzene (1×10^{-4} M) in hydrochloric acid of varying concentrations are presented in Figure 1. The reactions were carried out at 25° in cuvettes with a 1-cm light path. Though the over-all reaction is undoubtedly complex, the decrease in absorbance fol-

lowed first-order kinetics through 70% or more of the reaction in each case. These experiments show that the rate depends upon both the hydrogen ion concentration and the chloride ion concentration. A sequence of reactions initiated by attack of chloride ion on a protonated nitrobenzene in the excited state is an attractive possibility. It may be noted that a high concentration of nucleophile (Cl⁻ > 6 M for appreciable rate) is required, in contrast to the substitutions involving attack of hydroxide,[3,4] pyridine,[3] and cyanide[1] on photoexcited nitroanisoles, which proceed readily at nucleophile concentrations in the range of 0.01 to 0.001 M. The reaction of the nitroaromatics with hydrochloric acid bears a formal resemblance to photoinduced conversion of azobenzene in acetyl chloride to N,N'-diacetyl-4-chlorohydrazobenzene.[5]

(4) E. Havinga and R. O. deJong, *Bull. Soc. Chim. Belges*, **71**, 803 (1962); R. O. deJong and E. Havinga, *Rec. Trav. Chim.*, **85**, 275 (1966).
(5) G. E. Lewis and R. J. Mayfield, *Tetrahedron Letters*, 269 (1966).

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The Reaction of Trifluoromethyl Ketones and Trialkylphosphines

Sir:

We wish to report that the reaction of aryl trifluoromethyl ketones with *n*-trialkylphosphines yields olefins in which the carbonyl oxygen of the fluoro ketone is replaced by the alkenyl group of the trialkylphosphine.[1] To the best of our knowledge, this is the first reported example of olefination in the reaction between a ketone and a trialkylphosphine. Thus, olefins I and II were prepared in yields of 43 and 64%

$RCOCF_3 + (n\text{-}C_4H_9)_3P \longrightarrow$

I, R = C_6H_5
II, R = $p\text{-}CH_3C_6H_4$
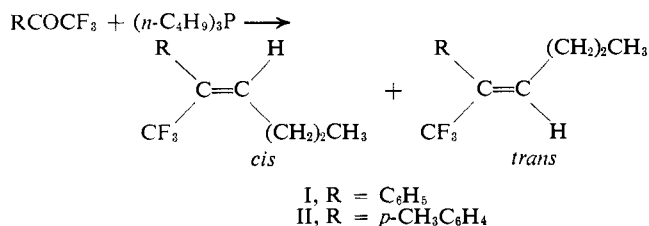
(based on starting ketone), respectively, by allowing equimolar quantities of trifluoroacetophenone and *p*-tolyl trifluoromethyl ketone to react with tri-*n*-butylphosphine in refluxing *n*-hexane for 20 hr.[3] In both cases a mixture of *cis* and *trans* olefins were

(1) In contrast to the formation of olefins in these reactions, Middleton[2] has observed only formation of difluoro-*n*-tributylphosphorane when hexafluorothioacetone dimer and tri-*n*-butylphosphine were allowed to react.
(2) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).
(3) Fuqua and co-workers[4] in an attempt to prepare 2-phenylpentafluoropropene by the Wittig reaction of difluoromethylenetri-*n*-butylphosphorane and trifluoroacetophenone obtained instead 1,1,1-trifluoro-2-phenyl-2-hexene (I) in low yields when tri-*n*-butylphosphine, sodium chlorodifluoroacetate, and trifluoroacetophenone were allowed to react in N-methyl-2-pyrrolidone. To account for these results, these workers proposed a mechanism based on analogous results with cyclohexanone, *n*-heptaldehyde, and acetophenone which involved rearrangement of the initial difluoromethylene ylide. Apparently, however, the use of sodium chlorodifluoroacetate was not necessary in this particular reaction of tri-*n*-butylphosphine and trifluoroacetophenone, which is a special case.
(4) S. Fuqua, G. W. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 2543 (1965).

obtained (*cis:trans* = 1:3). The pure geometrical isomers were separated by preparative gas chromatography and the structure assignments were made as follows: *trans* (I) gave an elemental analysis consistent with the molecular formula $C_{12}H_{13}F_3$. *Anal.* Calcd: C, 67.30; H, 6.07. Found: C, 67.06; H, 6.33. This isomer showed C=C absorption in the infrared at 5.99 μ. The assignment of the *trans* structure (*trans*-R,H) was made on the basis of the proton nmr spectrum. The 60-Mc spectrum of this isomer (relative to TMS as an internal standard) showed a phenyl singlet (area 5) at δ 7.26, a methyl triplet (area 3) at δ 0.83, a complex multiplet (area 4) at δ 1.08–2.17 for the methylene protons, and a triplet (area 1) for the vinyl proton at δ 6.40 ($J_{H,H}$ = 7 cps). Further resolution of this vinyl proton triplet gave a well-resolved quartet with J_{H,CF_3} = 1.4–1.5 cps characteristic of *cis* coupling of the trifluoromethyl group and a vinyl proton. *cis*-I also gave a satisfactory elemental analysis for the molecular formula $C_{12}H_{13}F_3$ (*Anal.* Found: C, 67.18; H, 5.96) and showed C=C absorption at 6.03 μ in the infrared. The proton nmr spectrum of this isomer showed a phenyl singlet (area 5) at δ 7.24, a methyl triplet (area 3) at δ 0.99, a broad multiplet (area 4) at δ 1.2–2.2 for the methylene protons, and a triplet (area 1) at δ 5.96 ($J_{H,H}$ = 7 cps) for the vinyl proton consistent with the assigned structure. Further resolution of the vinyl triplet gave only a poorly resolved quartet with an estimated J_{H,CF_3} = 0.7 cps characteristic of a *trans* coupling of the trifluoromethyl group and a vinyl proton. The assignment of *cis* or *trans* geometry for these isomers was based on the magnitude of their J_{H,CF_3} coupling constants. Previous workers[5,6] have reported J_{H,CF_3}-(*cis*) of 1.2–2 cps and J_{H,CF_3}(*trans*) of ~0 cps for coupling of a trifluoromethyl group and a vinyl proton. The magnitude of J_{H,CF_3} in this case was in good agreement with these values and was used to make the isomer assignments. Similar designations were employed in assigning structures in the *p*-tolyl case (II).

In contrast to the facile reaction of aryl trifluoromethyl ketones with tri-*n*-butylphosphine to produce olefins, *n*-heptaldehyde, benzaldehyde, and acetophenone did not react with tri-*n*-butylphosphine under these conditions and the carbonyl components could be recovered quantitatively from the reaction mixture. This behavior suggests that the enhanced reactivity of the trifluoromethyl ketone is in most part due to the electron-withdrawing ability of the trifluoromethyl group enhancing the electrophilic character of the carbonyl carbon.

Extension of this reaction sequence to other phosphines indicated that this transformation of fluoro ketones to olefins is a general reaction for trialkylphosphines. For example, under similar conditions as described above, tri-*n*-octylphosphine and trifluoroacetophenone gave a 55% yield of 1,1,1-trifluoro-2-phenyl-2-decene (III) (*cis:trans* = 1:2.6). Assignment of the *cis* or *trans* structure was again made on the basis of the magnitude of J_{H,CF_3}. The proton nmr spectrum of *trans*-III gave a triplet of quartets at δ 6.45 for the vinyl proton with J_{H,CF_3} = 1.5 cps, in

(5) D. J. Burton, R. L. Johnson, and R. T. Bogan, *Can. J. Chem.*, **44**, 635 (1966).
(6) W. R. Cullen and W. R. Leeder, *Inorg. Chem.*, **5**, 1004 (1966), and references contained therein.