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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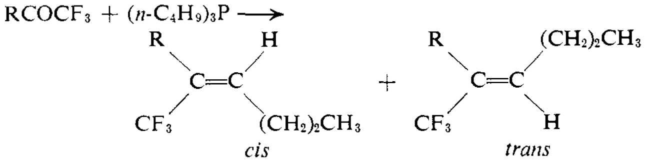
The Reaction of Trifluoromethyl Ketones and Trialkylphosphines

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% (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 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).



I, R = C_6H_5
II, R = $p\text{-}CH_3C_6H_4$

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

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(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).

(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.

agreement with *cis*-CF_3,H coupling, and *cis*-III gave a triplet at δ 5.97 for the vinyl proton. Increased resolution of this triplet showed only a poorly resolved quartet with $J_{H,CF_3} < 0.7$ cps, in agreement with *trans*-CF_3,H coupling.

In contrast to the behavior of trialkylphosphines in these reactions, triphenylphosphine failed to react with trifluoroacetophenone under these conditions. The recent report by Stockel,[7] who obtained 2,2-dihydro-2,2,2,triphenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxopholane from the reaction of triphenylphosphine and hexafluoroacetone, illustrates the subtle nature of this reaction and the slight changes in the electrophilic character of the carbonyl which influence the nature of the products obtained.

Although a serious mechanistic interpretation of this transfer reaction must await further work, the reaction sequence may be similar to that proposed earlier by Mark[8] for the reaction of phosphorus triamides with aldehydes which involved nucleophilic attack by the phosphorus at the carbonyl site to produce an intermediate of the type $(R'_2N)_3P^+CH(R)O^-$. In the present study, a similar type of intermediate is conceivable by attack of phosphorus on the carbonyl carbon to produce the intermediate $R_3P^+C(C_6H_5)R_fO^-$, which could then abstract a proton from an α-methylene group to give an ylide of the type $R_2P^+C(C_6H_5)R_fOHC^-HR_{n-1}$ which then subsequently reacts with another ketone molecule in a normal Wittig reaction to produce the isolated olefins.[9] Additional work is in progress to determine the scope and mechanism of this novel transfer reaction.

Acknowledgment. This work was supported in part by a grant from the Public Health Service (GM 11809-03) for which grateful acknowledgement is made.

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[7] R. F. Stockel, *Tetrahedron Letters*, 2833 (1966).

[8] V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).

[9] An apparent flaw in this argument, as pointed out by a referee, is the high yield of olefins (*i.e.*, 55 and 64%) which, based on the predicted stoichiometry, could be a maximum of only 50% based on ketone. However, the decomposition of disubstituted phosphinyl alcohols[10,11] of the type $R_2P(O)C(OH)R'R''$ and $R_2P(S)C(OH)R'R''$ are not without precedent, and the phosphinyl alcohol generated in this case could conceivably break down to regenerate the ketone which could react again.

[10] R. C. Miller, C. D. Miller, W. Rogers, Jr., and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957).

[11] G. Peters, *J. Org. Chem.*, **27**, 2198 (1962).

[12] NASA Trainee 1964–1966.

[13] NSF Trainee 1965–present.

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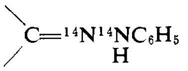
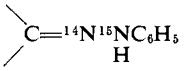
Rearrangement of Isotopically Labeled Diazonium Salts

Sir:

The rearrangement of benzenediazonium and *p*-toluenediazonium-α-^{15}N salts to the corresponding β-^{15}N salts accompanying the hydrolysis has been described.[1] We now report data on several new cases and evidence bearing on the kinetic order, and find a close connection between the rearrangement and the hydrolysis. We further confirm the earlier results and cast some question on a recent report by Bose and Kugajevsky.[2] They prepared hydrazones from benzenediazonium-α-^{15}N ion and showed that the proton resonance spectrum associated with the structure I did not appear after partial hydrolysis of the diazonium salt; the spectrum of the derivative of the starting material, II, was clearly distinguished from that of I.


I


Ia


II

They concluded that the isotopic rearrangement did not occur and that our results were the result of an experimental error. The spectrum of compound Ia, the rearrangement product of II, was not determined and was assumed to be the same as I. We believe that this is the source of the discrepancies, and that the NH proton in Ia may be sufficiently split by the neighboring ^{15}N so that the absorption indeed does not overlap that of the proton in I.

Table I shows the earlier results together with new results obtained by a different experimenter and using a different mass spectrometer with a different operator. The earlier results are quantitatively confirmed.[3] It is also seen that the reaction is general and the rate is between 1 and 4% of that of the hydrolysis in all the compounds tested. Over this same range of compounds the rates of hydrolysis vary by a factor of over 20,000, and do not correlate with the rates of any other reaction or with the Hammett σ, so this close similarity of the rates suggests an intimate relationship between the two mechanisms. This relationship follows also from the previously reported temperature independence of the relative rates.

Table I. Extent of Rearrangement of Substituted Benzenediazonium Salts Accompanying 80% Hydrolysis

Substituent and initial α-^{15}N content, %	% β-^{15}N from secondary N_2	Average p,[g] %	R[h]
p-CH_3,[a] 97	1.45	4.73	0.031
p-CH_3,[a,b] 99.3	1.58	4.60	0.029
p-OCH_3,[c] 97	1.72	5.82	0.038
p-Cl,[d] 99	1.26	3.36	0.023
m-CH_3[e] 99	1.08	2.87	0.018
None,[b,f] 99.3	0.91	2.10	0.014

[a] At 48.8°. [b] From ref 1. [c] At 90.5°. [d] At 79.8°. [e] At 40.1°. [f] At 35°. [g] Average of the fraction of isomerization from the secondary nitrogen and from the nitrogen from the reduction of the aryl azide with arsenite; see ref 1. [h] Ratio of the rearrangement and hydrolysis rates.

The insensitivity of this reaction to changes of condition is alternatively explicable in terms of a systematic error in either the degradation or the analysis. Analytical error is improbable because of the reproducibility of the analysis between the two instruments, because the nitrogen samples were shown in every case to be free from contamination from other gases

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[1] E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.*, **86**, 32 (1964).

[2] A. K. Bose and I. Kugajevsky, *ibid.*, **88**, 2325 (1966).

[3] We do not in any way doubt the original experimental results but we now believe that the argument for the intermediate spirocyclic diazirine cation (E. S. Lewis and J. M. Insole, *ibid.*, **86**, 34 (1964)) was based on a fortuitous coincidence of rate and tracer data rather than a necessary relationship.