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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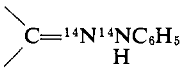
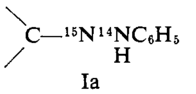
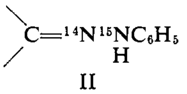
Rearrangement of Isotopically Labeled Diazonium Salts

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.

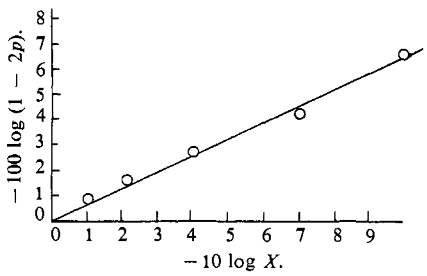

Figure 1.

except for minor air contamination for which trivial corrections were made, and finally because the natural abundance level agreed with the accepted value in cylinder gases as well as in air and various blanks made in the course of the study. Among these blanks were several degradations of α-labeled diazonium salts which had not been subjected to partial hydrolysis; these gave only natural abundance of ^{15}N in the β position within the experimental error, showing that the degradation was effective. The extent of rearrangement can be quantitatively related to the extent of hydrolysis by the equations derived previously,[1] assuming that the reaction is kinetically first order and neglecting the isotope effect (this is certainly larger than was estimated by direct rate measurement, as shown by reliable competitive methods,[4] but still not large enough to cause concern in this connection). A convenient form of the relationship is the readily derived eq 1, in which $R = k_{\text{rearr}}/k_{\text{hydrol}}$ and p is the fraction of the label in the β position when the fraction of remaining total diazonium salt is x.

$$2R \log x = \log (1 - 2p) \qquad (1)$$

Figure 1 shows a plot of log (1 − 2 p) *vs.* log x for p-toluenediazonium ion at extents of completion from 20 to 90%, and the line is drawn from eq 1 with $R = 0.033$, in satisfactory agreement with $R = 0.029$ from many runs to 80% completion. The satisfactory fit to the line demonstrates the first-order kinetics and provides as well information not easily ascribed to experimental error.[5]

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(4) L. L. Brown and J. S. Drury, *J. Chem. Phys.*, **43**, 1688 (1965).

(5) A referee comments that a minor isotopically rearranged product other than diazonium ion may be responsible for these results. If so, this substance must have the following characteristics in common with the diazonium ion $Ar^+N{\equiv}^{15}N$: a reaction with azide ion to give no ^{15}N in primary nitrogen, giving secondary nitrogen after warming, and leaving a product which gives nitrogen with arsenite; the relative yields must be similar; a very similar rate of destruction, necessitated by the kinetics, and closely similar activation energy for formation and destruction; all the above similarities are unaltered when the substitution on the diazonium ion is changed. We feel that this identification is compelling.

(6) R. E. H. thanks the National Aeronautics and Space Administration for a traineeship; we also thank the Robert A. Welch Foundation for support of much of this work.

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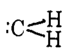
Evidence for a Novel Metal–Carbene System

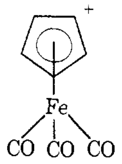
Sir:

It has recently been recognized that carbene (I) may be capable of acting as a ligand in certain organo-transition metal complexes. The lone pair electrons in



$:C{<}^{H}_{H}$

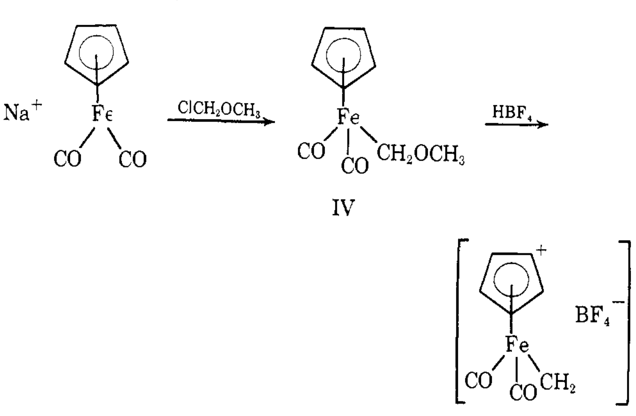
I



II

I could act as a donor pair and the vacant p_z carbon orbital would be available for back-donation of electrons from the metal. The species could thus be classified with carbon monoxide and triphenylphosphine as far as donor–acceptor capabilities are concerned and could, in principle, replace such ligands in their stable complexes. The validity of this reasoning has recently been convincingly demonstrated by Fischer and Maasböl[1] through the isolation of methoxymethylcarbene–tungsten pentacarbonyl. We now wish to report evidence for the formation of a very reactive metal complex containing the parent unsubstituted carbene ligand.

Salts of the cyclopentadienyliron tricarbonyl cation (II) have been isolated[2] and the above reasoning suggests that the cyclopentadienyliron dicarbonyl carbene cation (III) might also be stable. Reaction of the sodium salt of the cyclopentadienyliron dicarbonyl anion with chloromethyl methyl ether produced (methoxymethyl)cyclopentadienyliron dicarbonyl[3] (IV). Ether cleavage of IV with acids would be expected to yield the carbene complex III if the latter were to be stable. Complex IV reacted rapidly with HBF_4 and both cyclopentadienylmethyliron dicarbonyl (V) and the cyclopentadienylethyleneiron dicarbonyl cationic complex (VI) were isolated as products. Both V and VI are known species,[2a,4] and their formation can be reasonably formulated through intermediacy of the cation III. When conducted at 0° in the presence of cyclohexene, the reaction of IV with HBF_4 produced norcarane (46% yield based on IV) together with other species, predominantly II and V. The methylene transfer reaction



IV

III

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(1) (a) E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964); (b) O. S. Mills and A. D. Redhouse, *ibid.*, **77**, 1142 (1965).

(2) (a) E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961); (b) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

(3) The elemental analysis and nmr spectrum of this new product agree with the proposed formulation.

(4) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956). (b) In a recent personal communication Professor M. L. H. Green has informed us that he has also observed compounds V and VI to be produced upon treatment of IV with acids; he also interprets this reaction as proceeding *via* the carbene complex III.