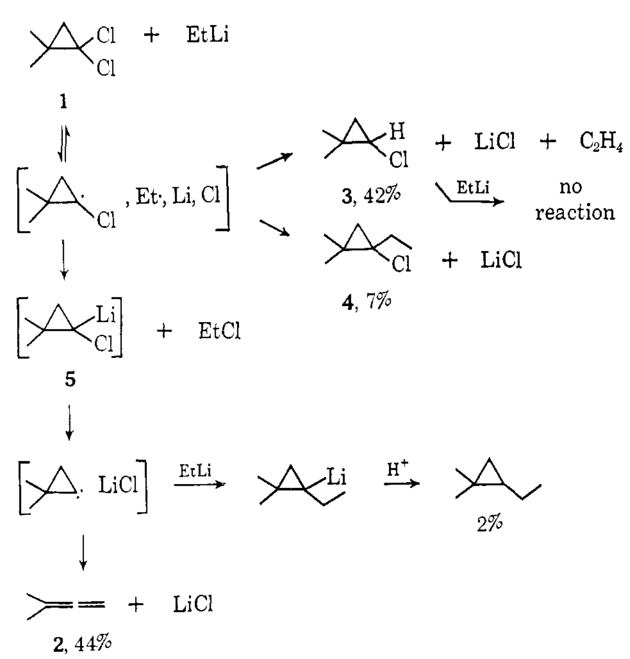
Scheme I



radical, is transferred during a radical disproportionation, and exhibits enhanced absorption in the new molecule. Specifically, the α-halo proton in **3** probably was polarized in the ethyl radical before hydrogen atom transfer occurred.

If the idea of the intermediacy of **5** is valid, then, since polarization continues into the allene, there is a possibility of direct observation of CIDNP from **5**. Some of the unassigned emission and enhanced absorption between δ 0.17 and 0.83 may be tentatively assigned to **5**, but we have not yet been able to prepare **5** at low temperatures for a comparison absorption spectrum. The fact that CIDNP is observed in **2** places the proton relaxation time (a few seconds) as an upper limit on the lifetime of **5** under the reaction conditions.[8]

When *n*-butyllithium or *t*-butyllithium reacts with **1**, polarization can be observed from the protons in the olefin formed by disproportionation.[9] This polarization is of a single sign for a particular proton at a particular time (*e.g.*, the vinyl protons of isobutylene show only emission), distinctly different from the isobutylene formed in the reaction of *t*-butyllithium and *n*-butyl bromide[5] where the vinyl protons exhibit both positive and negative polarization effects.

The observation of CIDNP phenomena seems to offer continued promise as a technique for the investigation of unstable intermediates which result from one-electron transfers.

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[8] The polarization of nuclei in **2** may also arise from the intermediacy of a triplet-state carbenoid species in the reaction of **5**. Such a double "paramagnetic pulse" seen by the nuclei on the route from **1** to **2** may be difficult to establish in the absence of isolation of **5** as a stable species. Nuclear polarization also may arise from the intermolecular dipolar interaction generated during nonreactive encounters between free radicals and proton-containing molecules in solution (K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance*, **3**, 79 (1968). However, strong positive polarization of solvent protons has not been observed (to our knowledge) in dynamic nuclear polarization experiments on electromagnetically pumped solutions of neutral free radicals. The positive polarization seen in the present example requires an unprecedented time-dependent scalar coupling between the unpaired electron of a neutral free radical and the protons of surrounding molecules, if it is to occur by intermolecular interaction.

[9] The absorption of the ethylene in Figure 1b is more intense than in the product (Figure 1c), but some of the diminution of signal may be from the escape of ethylene from solution; polarization has not been established in this case.

[10] National Center for Air Pollution Control Special Fellow (predoctoral).

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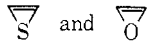
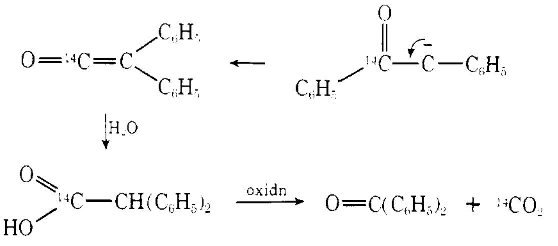
The Mechanism of the Wolff Rearrangement

Sir:



MO calculations recently performed by us on the three-membered strained ring systems predict a singlet ground state with low stability for both species. A similar result was reported earlier for the sulfur compound by Zahradnik.[1] We could experimentally verify this prediction for thiirene by observing the transient existence (with half-lives of up to several seconds) of thiirene and its homologs in the gas-phase addition reactions of sulfur atoms to acetylenes and in the photolysis of 1,2,3-thiadiazole.[2]

Oxiirene, however, has not yet been detected. It has been postulated as an intermediate in the peroxyacid oxidations of acetylenes[3] and considered in the decompositions of α-diazo ketones. Franzen[4] has attempted to elucidate the mechanism of the Wolff rearrangement, the isomerization of α-keto carbenes to the ketene structure, by using ^{14}C-labeling techniques. Photolysis and thermolysis of [^{14}C]azibenzil were carried out in dioxane–water–triethylamine and dioxane–water solutions, and the position of the ^{14}C atom in the resulting diphenylacetic acid was determined by oxidative decarboxylation followed by measurement of the radioactivity of the carbon dioxide. It was concluded that oxiirene is not an intermediate and the reaction proceeds *via*



since all radioactivity appeared in the carbon dioxide product. This result agreed with that of a similar study reported earlier by Huggett, *et al.*[5] Thus for these reasons it has since been generally accepted that the Wolff rearrangement does not involve the oxiirene intermediate.[6]

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[1] R. Zahradnik, *Advan. Heterocyclic Chem.*, **5**, 14 (1965).

[2] O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 4805 (1967).

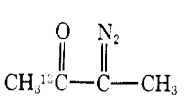
[3] J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964); R. N. McDonald and P. A. Schwab, *ibid.*, **86**, 4866 (1964).

[4] V. Franzen, *Ann.*, **614**, 31 (1958).

[5] C. Huggett, R. T. Arnold, and T. I. Taylor, *J. Am. Chem. Soc.*, **64**, 3043 (1942).

[6] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1960; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

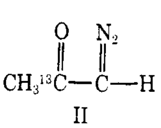
In a previous communication[7] we reported that the Wolff rearrangement extends to α-diazo esters as well, and the reaction occurs not only in solutions but also in the gas phase. The ketene formed subsequently undergoes *in situ* photolysis to yield carbon monoxide and a secondary carbene. The gas-phase reaction offers the distinct advantage that it is free from complications arising from possible solvent–carbene interaction and intervention of ionic intermediates. We therefore reexamined the reaction in the gas phase, using a symmetrical and an asymmetrical ^{13}C-labeled α-diazo ketone, both containing 55% ^{13}C.



$CH_3{}^{13}C(=O)-C(=N_2)-CH_3$

I

and



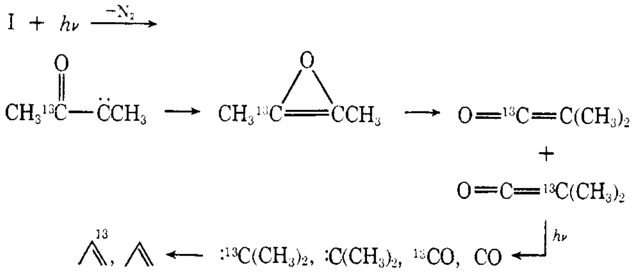
$CH_3{}^{13}C(=O)-C(=N_2)-H$

II

The photolysis of *ca.* 5 torr of I with 5 torr of 1-propanol (from which it could not be separated) was carried out using a 140-W lamp with a 2200 Å cutoff filter. Three major products resulted, N_2 and CO in equal yields and propylene, along with smaller amounts of ethane, ethylene, propane, and methane. The combined yield of the latter four products was about 40% of that of propylene.

High-resolution (MS-9) mass spectrometric analysis gave for the isotopic distribution of carbon monoxide, after correction for incomplete ^{13}C labeling in the starting material, 51.8% ^{13}CO and 48.2% ^{12}CO. Isotopic analysis of the propylene gave 48% ^{13}C-labeled propylene and 52% normal propylene. The ethylene product was also partially labeled, but the ethane contained no ^{13}C.

These results require the intervention of the oxiirene structure in the mechanism

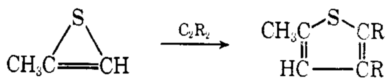


The precursor of ethane and methane is the methyl radical, and of ethylene, the vinyl radical, formed by some cracking reactions.

The photolysis of *ca.* 10 torr of II afforded N_2 and CO in not quite equal yields together with small amounts of H_2 and CH_4. The major component of the condensable fraction was ethylene, with acetylene (20%) and a few per cent each of ethane, propane, and propylene.

Isotopic analyses gave $^{13}CO = 84\%$ and $CO = 16\%$. Also 27% of the ethylene and 23% of the acetylene were ^{13}C labeled.

Thus we conclude that oxiirene is an intermediate in the gas-phase Wolff rearrangement of the α-keto carbenes from I and II. With the symmetrical dimethyloxiirene all the initially formed carbenes undergo cyclization, and ring opening is equally possible on either side. With the asymmetrical monomethyloxiirene, ring opening preferentially occurs on the hydrogen side, a trend which has been observed with thiirene.



The exact cause of the discrepancy with earlier results is not clear. It may be due to solvent effects, substituent effects, pressure effects, or to a difference in the excess energy of the initial carbene. It is hoped that further studies currently in progress will shed light on these questions.

Preparation of I. $CH_3{}^{13}COONa$ (Merck 55% ^{13}C) was treated[8] with $POCl_3$ to give $CH_3{}^{13}COCl$ which was further treated with a 1-propanol–ether solution of diazoethane.[9] The excess solvent was evaporated and the residue distilled under vacuum. Ir and mass spectrometric analyses indicated the presence of about 50% 1-propanol, which could not be removed by distillation.

Preparation of II. The $CH_3{}^{13}COCl$ was allowed to react with excess diazomethane and after the solvent was removed by evaporation II was subjected to low-temperature distillation.

Both I and II contained 55% ^{13}C.

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(7) O. P. Strausz, T. DoMinh, and H. E. Gunning, *J. Am. Chem. Soc.*, **90**, 1660 (1968).

(8) D. T. Mowry, *ibid.*, **66**, 371 (1944); W. N. Haworth, H. Gregory, and L. F. Wiggins, *J. Chem. Soc.*, 490 (1946).

(9) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

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The Aquorhodium(II) Ion

Sir:

Extensive work[1] on the polarographic behavior of aquo, halo, and ammine complexes of rhodium(III) has failed to yield unequivocal proof of the existence of the corresponding rhodium(II) complexes. Several compounds containing Rh(II) have been prepared, among them $Rh(CH_3CO_2)_2$[2,3] together with related substances[4,5] and a number of compounds in which back-bonding ligands are coordinated to Rh(II).[6,7]

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(1) See, for example, P. Beran and J. Dolezal, *Collect. Czech. Chem. Commun.*, **23**, 608 (1958); D. Cozzi and F. Pantani, *J. Inorg. Nucl. Chem.*, **8**, 385 (1958); M. B. Bardin and V. I. Shapiro, *Uch. Zap. Kishinevsk. Gos. Univ.*, **68**, 64 (1963); R. J. Magee and W. H. Douglas, *J. Inorg. Nucl. Chem.*, **26**, 1707 (1964); G. Van Loon and J. A. Page, *Talanta*, **12**, 227 (1965); R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 4107 (1965).

(2) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(3) L. A. Nazarova, I. I. Chernyaev, and A. S. Morozova, *Russ. J. Inorg. Chem.*, **10**, 291 (1965).

(4) I. I. Chernyaev, E. V. Shenderetskaya, A. G. Maiorova, and A. A. Koryagina, *ibid.*, **10**, 290 (1965).

(5) S. Cenini, R. Ugo, and F. Bonati, *Inorg. Chim. Acta*, **1**, 443 (1968).

(6) F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc., N. S. Wales*, **75**, 122, 127, 140 (1942); **76**, 129, 133, 275 (1942); **78**, 266 (1946).

(7) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).