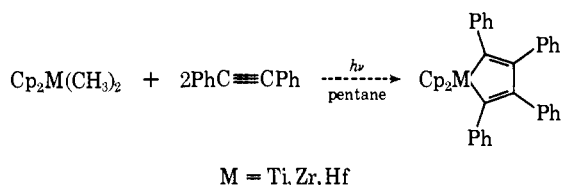Titanocene produced by this photochemical process can be obtained in yields of >90% during photolysis periods of 2–3 hr, while zirconocene and hafnocene are obtained in lower yields and require correspondingly longer periods of irradiation. Titanocene prepared in this manner appears black in the solid state, in contrast to the green color of titanocene prepared by other methods.[10,11] Zirconocene and hafnocene obtained by the photolytic method are dark brown and gray, respectively, in contrast to the dark purple colors described for these metallocenes prepared by the sodium-naphthalene reduction of the corresponding metallocene dichlorides.[5,12] All three metallocenes are pyrophoric in air, the hafnium analog being especially so.

When the dimethyl derivatives of titanocene, zirconocene, and hafnocene are photolyzed in solution in the presence of acetylenes, metallocycles are the major products. Photolysis in the presence of diphenylacetylene, for example, produces the corresponding metallocycles in yields of 35–50%. All metallocycles were characterized by elemental analysis, mass spectrometry, and proton nmr spectrometry. The green

$$Cp_2M(CH_3)_2 \ + \ 2PhC{\equiv}CPh \ \xrightarrow[\text{pentane}]{h\nu} \ Cp_2M\langle\text{C(Ph)=C(Ph)-C(Ph)=C(Ph)}\rangle$$

M = Ti, Zr, Hf

titanium and the orange zirconium metallocycles have been previously described;[5,13–15] however, the present photochemical route offers a very convenient new route to these products. The yellow hafnocycle has not yet been characterized, and attempts to prepare it by other methods have been largely unsuccessful.[5] Under the photochemical conditions employed, the methyl radicals react not only to produce methane but also undergo reaction with the diphenylacetylene present to yield a variety of other compounds, including cis- and trans-methylstilbenes (identified by proton nmr and mass spectrometry).[16]

The previously reported[4] bis(indenyl)metal dimethyl derivatives of titanium, zirconium, and hafnium show reactivities similar to their π-cyclopentadienyl analogs under photochemical conditions. Thus, photolysis of bis(indenyl)zirconium dimethyl in pentane proceeds with the liberation of methane and formation of the black pyrophoric product, bis(indenyl)zirconium. In contrast to the broad absorptions of the cyclopentadienyl ring protons in zirconocene, this new indenyl complex exhibits sharp, distinct signals for the protons of the five-membered and the six-membered rings at τ 3.8–4.2 and 2.4–3.2 ppm, respectively. Photolysis of

the bis(indenyl)metal dimethyl compounds in the presence of acetylenes likewise leads to metallocycles containing indenyl substituents.

In solution, all these bis(cyclopentadienyl) and bis(indenyl) derivatives of titanium, zirconium, and hafnium show very high reactivities toward carbon monoxide, nitric oxide, nitrogen, hydrogen, and olefins as well as toward acetylenes. For example, black titanocene reacts with carbon monoxide in solution at room temperature and atmospheric pressure to form $Cp_2Ti(CO)_2$ in essentially quantitative yield. Zirconocene and hafnocene also react with carbon monoxide under these conditions, and further studies along these lines are in progress. Black titanocene also reacts with hydrogen chloride in benzene solution to form Cp_2TiCl_2 as the major product and with molecular nitrogen in tetrahydrofuran solution at room temperature to form a dark purple, nitrogen-containing complex which can be isolated as a solid. It is possible that black titanocene obtained in our studies may be similar to a metastable form of titanocene prepared in solution but not isolated by Brintzinger, et al.[8,17] Several of these photochemically produced metallocenes have also been found to be highly active catalysts for the polymerization of α-olefins. Further investigations concerning the structures and chemical behavior of these compounds as well as extensions to other σ-organotransition metal systems are in progress and will be described in subsequent publications.

(17) R. H. Marvich and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2046 (1971).

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Intermolecular Insertion Reactions of Phosphoryl Nitrenes

Sir:

Nitrene insertion has been used in affinity labeling of enzymes.[1] It is also an attractive reaction for application in remote oxidation,[2] in which it could be directed to the functionalization of unactivated positions in a molecule by geometric proximity constraints. However, most nitrenes undergo intramolecular rearrangement processes[3] rather than insert into nearby C–H bonds. Even those nitrenes derived from the class[4] referred to as "starre" azides, which supposedly are resistant to intramolecular rearrangement, nonetheless

(10) K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, **654**, 8 (1962).
(11) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1138 (1966).
(12) G. W. Watt and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 5926 (1966).
(13) M. E. Vol'pin, V. A. Dubovitski, O. V. Nogina, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **151**, 1100 (1963).
(14) K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1178 (1966).
(15) E. H. Braye, W. Hübel, and I. Caplier, *J. Amer. Chem. Soc.*, **83**, 4406 (1961).
(16) M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, **15**, 139 (1968).

(1) J. R. Knowles, *Accounts Chem. Res.*, **5**, 155 (1972).
(2) R. Breslow, *Chem. Soc. Rev.*, **1**, 553 (1972); R. Breslow, S. Baldwin, T. Flechtner, P. Kalicky, S. Liu, and W. Washburn, *J. Amer. Chem. Soc.*, **95**, 3251 (1973).
(3) W. Lwowski in "Nitrenes," W. Lwowski, Ed., Wiley, New York, N. Y., 1970.
(4) T. Curtius, *Z. Angew. Chem.*, **27**, 213 (1914).

give only moderate yields of insertion products into neighboring molecules. Thus photolysis of ethyl azidoformate in cyclohexane solvents gives only a 51% yield of the product from insertion into the cyclohexane along with 12% of hydrogen abstraction and other unidentified material,[5] and thermolysis of p-toluenesulfonyl azide in cyclohexane similarly leads to only a 58% yield of the insertion product along with dark, tarry materials.[6]

Curiously, although phosphoryl azides are a well-known class of compounds,[7] the properties of the derived nitrenes have been little investigated.[8] We now wish to report that as hoped some members of this class are very resistant to a rearrangement which would produce the rather weak 3p-2p P-N π bond; these nitrenes thus lead to excellent yields of products from attack on neighboring molecules. At the same time, it turns out that this class of nitrenes shows the lowest reported chemical selectivity among different types of C-H bonds, and thus it is particularly suitable for applications in which geometrical proximity control is to be the dominant factor.

Photolysis[9] of a 10^{-2} M solution of diethylphosphoryl azide[7a, 10] (1) in cyclohexane solution led to the production[11] of the diethyl cyclohexylphosphoramidate[12] (2) in 88% yield and diethylphosphoramide[12] (3) in 12% yield. Both of these products are derived from attack on the solvent, and no other materials, specifically no materials derived from rearrangement of the diethylphosphorylnitrene, could be detected. Photolysis of diphenylphosphoryl azide[7b] (4) in cyclohexane did involve some side reactions, but a 67% yield of the diphenyl cyclohexylphosphoramidate (5) from insertion into the solvent was still obtained. By contrast, photolysis of phenyl azidoformate in cyclohexane afforded only a 19% yield of the N-cyclohexylurethane from solvent insertion, along with other unidentified material apparently resulting from intramolecular processes.

$$(RO)_2PON_3 + cyclohexane \xrightarrow{h\nu}$$

$$(RO)_2PONHC_6H_{11} + (RO)_2PONH_2$$

| 1, R = Et | 2, R = Et | 3, R = Et |
| 4, R = phenyl | 5, R = phenyl | |

Relative selectivities of these nitrenes for various classes of C-H bonds were assessed in a standard way by photolysis in 2-methylbutane solution. From the photolysis of 1 we obtained the hydrogen abstraction product 3 in 7% yield and a mixture of four phosphoramidates[12,13] in 74% yield, resulting from insertion into the C-H bonds of the solvent. With diphenylphosphoryl azide the corresponding insertion products[12,13] were obtained in 65% yield. Careful glpc analysis,[11] calibrated with unambiguously synthesized samples, led to the relative reactivities indicated in Table I.

Table I. Selectivity of Nitrene Insertion into C-H Bonds of 2-Methylbutane

| Azide | Reactivity per C-H Bond | | |
	Tertiary	Secondary	Primary
(EtO)₂P(O)N₃[a]	6.0	4.3	1
(PhO)₂P(O)N₃[a]	3.4	1.2	1
EtOC(O)N₃[b]	34	9	1
tBuC(O)N₃[b]	160	9	1
C₆H₅N₃	140–280	7	1

[a] This study. [b] From Table IV, p 201 in ref 3.

$$(RO)_2PON: + (CH_3)_2CHCH_2CH_3 \longrightarrow (RO)_2PONHR'$$

6, R' = –CH₂CH(CH₃)CH₂CH₃
7, R' = (CH₃)₂CHCH₂CH₂–
8, R' = (CH₃)₂CHCH(CH₃)–
9, R' = CH₃CH₂C(CH₃)₂–
a, R = Et; b, R = phenyl

The analytical column clearly resolved primary insertion products (6 and 7) from secondary (8) and tertiary (9) but did not clearly separate 6 from 7. Since the detector sensitivity was the same for 6 and 7, this total peak was used (statistically corrected) for the table entry. As this table shows, the phosphorylnitrenes are enormously less selective among C-H bonds than are nitrenes substituted with carbonyl or phenyl groups.

Further evidence for the highly reactive and unselective nature of the phosphorylnitrenes was obtained by irradiation of 1 in tert-butyl alcohol. Ethyl azidoformate is reported[14] to afford only O-H insertion product when it is photolyzed in tert-butyl alcohol, but in the phosphoryl case we obtain not only the O-H insertion product 11 and some hydrogen abstraction product 3 but also a substantial yield of a product (10)[12,13] from insertion into the C-H bond of a methyl group.

$$(EtO)_2PON: + tert\text{-butyl alcohol} \longrightarrow$$

$$(EtO)_2PONHCH_2C(CH_3)_2OH + (EtO)_2PONHOCMe_3 + 3$$

| 10 | 11 | (27%) |
| (35%) | (33%) | |

This very low selectivity may be a reflection of steric effects or of poor stabilization of the nitrene by bonding with the neighboring phosphoryl group, and this same poor stabilization of the nitrene could explain the remarkable thermal stability[8a] of phosphoryl azides[15] compared with some other azide derivatives. The decreased tendency for intramolecular migration reactions is also presumably related to the weakness of P-N

(5) W. Lwowski and T. W. Mattingly, J. Amer. Chem. Soc., 87, 1947 (1965).

(6) M. F. Sloan, D. S. Breslow, and W. B. Renfrow, Tetrahedron Lett., 2905 (1964).

(7) (a) F. S. Scott, R. Riordan, and P. D. Morton, J. Org. Chem., 27, 4255 (1962); (b) T. Shioiri, K. Ninomiya, an S. Yamada, J. Amer. Chem. Soc., 94, 6203 (1972); (c) G. S. Hartley and D. W. Pound, U. S. Patent No. 2,649,464, Aug 18, 1953; (d) R. A. Baldwin, J. Org. Chem., 30, 3866 (1965).

(8) (a) W. T. Reichle, Inorg. Chem., 3, 402 (1964); (b) M. J. P. Harger, Chem. Commun., 442 (1971); (c) A. Zwierzak and S. Zawadzki, Tetrahedron, 29, 3899 (1973).

(9) Photolyses were performed using a 450-W medium-pressure Hanovia lamp with Vycor filter contained in a water cooled immersion well apparatus. Argon was bubbled through the solution for 2 hr prior to and during irradiation. Solutions were irradiated until ir analysis showed complete disappearance of the azide band at 2160 cm⁻¹.

(10) The extreme toxicity of diethylphosphoryl azide has been noted previously[7a] and confirmed by in vivo tests kindly performed for us by Hoffmann-LaRoche, Inc. However, with suitable precautions, we have encountered no difficulties in handling this material.

(11) Glpc analyses were performed using a Hewlett-Packard 5250 instrument equipped with flame ionization detector and a 9 ft × ⅛ in. 3% SE-30 column. Product yields were measured using an internal standard and are corrected for relative detector response.

(12) Photolysis products were identified by comparison of their spectroscopic properties and glpc retention times or tlc R_f values with authentic samples, prepared by treating (RO)₂P(O)Cl with an appropriate amine.

(13) These previously unreported phosphoramidates had nmr, ir, and high resolution mass spectra and/or elemental analyses fully in accord with the assigned structures. The compounds were oil except 7b, mp 48–49°; 8b, mp 53–55°; 9b, mp 36–39°.

(14) R. Kreher and G. H. Bockhorn, Angew. Chem. Int. Ed. Engl., 3, 589 (1964).

(15) Thermal decomposition of 1 and 4 required temperatures >220°.

double bonds, but this factor is not dominant in all situations. It is reported that pyrolysis of diphenylphosphinyl azide[8a] leads to phenyl migration, and migration of saturated carbon has also been observed.[8b] We find that a dimethylamino group attached to phosphorus also migrates readily in the corresponding nitrene. Thus, photolysis of bis(dimethylamino)phosphoryl azide (12)[7c] in cyclohexane afforded only a 7% yield of the product (13)[12,13] of insertion into the solvent. The remaining high molecular weight residue could not be directly identified, but its nature is indicated by the results of a photolysis of 12 in methanol. Again, the product did not involve direct attack of the nitrene on the solvent, but instead a product (14)[16] was obtained from trapping of a reactive rearrangement product by the methanol solvent. The intermediate metaphosphate derivative (15) would be expected to give high molecular weight material in the absence of such a trapping reagent.

$$(Me_2N)_2PON_3 \xrightarrow{h\nu} (Me_2N)_2PON: \xrightarrow{cyclohexane} (Me_2N)_2PONHC_6H_{11}$$
12   **13**
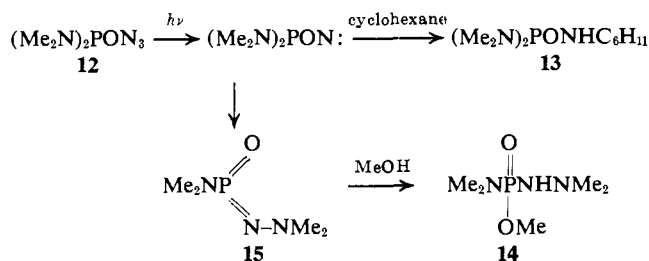
That dimethylamino, alkyl, or phenyl groups are able to migrate in situations in which alkoxyl and phenoxyl groups do not is not surprising, but it does suggest the limitations in the classes of compounds which can be utilized to afford nonrearranging highly reactive nitrene insertion reagents. Within this class of phosphorylnitrenes, however, are materials with particularly attractive potential for functionalizations utilizing proximity effects.

Acknowledgment. This work was supported by the National Institutes of Health.

(16) An authentic sample[13] of 14 was obtained by stepwise reaction of methyldichlorophosphate with dimethylamine and unsymmetrical dimethylhydrazine.
(17) NIH Postdoctoral Fellow, 1972–1974.

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Automerization of 6-Methylenebicyclo[3.2.1]oct-2-ene[1]

Sir:

As part of a study of the sigmatropic rearrangements of some biallylic systems,[2] we have examined the pyrolysis of 6-methylenebicyclo[3.2.1]oct-2-ene. During the course of this work, Hasselmann[3] reported a closely related thermal rearrangement of 6-methylenebicyclo-

(2) (a) J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 267, 269 (1973), and references cited there; (b) J. A. Berson, T. Miyashi, and G. Jones, II, *ibid.*, **96**, 3468 (1974).
(3) D. Hasselmann, *Tetrahedron Lett.*, (a) 3465 (1972); (b) 3739 (1973).

[3.2.0]hept-2-ene, deuterated either at C_7 (1a) or C_8 (1b), to 2-methylenebicyclo[2.2.1]hept-5-ene, 2a and 2b. In each case, the product of formal [1,3]-sigmatropic rearrangement predominated slightly (1a → 56% 2a and 44% 2b; 1b → 60% 2b and 40% 2a).

Three interpretations of these results were considered (Scheme I)[3b]: (1) a nearly equal competition between

Scheme I
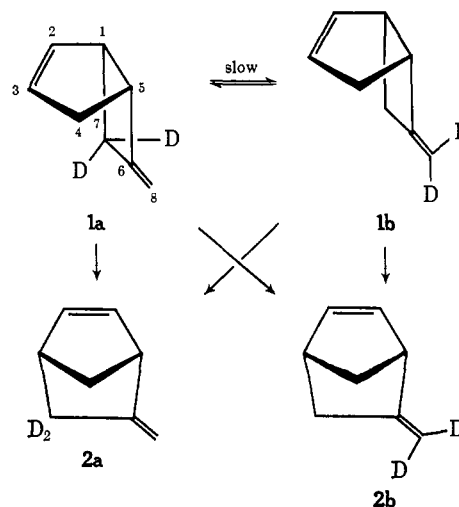
a [3,3]-sigmatropic (Cope) rearrangement (1a → 2b) and a [1,3]-sigmatropic rearrangement (1a → 2a); (2) a competition between a [1,3]-sigmatropic rearrangement and a diradical mechanism involving C_1–C_7 bond cleavage to give a freely rotating intermediate, with the sigmatropic rate constant about one-seventh (from 1a) or one-fifth (from 1b) as large as the diradical-forming rate constant; (3) cleavage of the C_1–C_7 bond to give a "not completely equilibrated" diradical, which for steric reasons cyclized preferentially at C_3–C_7 rather than at C_3–C_8.

The substrate in our work is 6-methylenebicyclo-[3.2.1]oct-2-ene-$3,9,9$-d_3 (3a), which can be synthesized with 0.91 D at C_3 and >1.96 D at C_9 in eight steps[4] from norborn-5-en-2-one. Molecule 3a is conceptually related to Hasselmann's 1a–b system by the insertion of a methylene group into the bridge bond (C_1–C_5 of 1a–b). This introduces diagnostically useful symmetry properties into the several conceivable automerization pathways.

Heating a neat, degassed sample of 3a at 308.6° causes the C_3 deuterium to become distributed between C_3 and C_1, while the C_9 deuterium becomes distributed between C_9 and C_7. The reaction is monitored by integration of the magnetic resonance signals of the protons at C_2(δ 6.04), C_3(δ 5.48), and C_9(δ 5.05) with a Jeol 100-MHz spectrometer. After six half-lives, the C_3 and C_9 proton signals, corrected for incomplete deuteration in 3a, have intensities of 50 ± 3% and 52 ± 3% of one and two protons, respectively. Aside from a minor side reaction which produces 1–10% of the endocyclic isomer of 3a, 6-methylbicyclo[3.2.1]octa-2,6-diene,[5] there are no other changes in the system.

(4) *Via* bicyclo[3.2.1]oct-2-en-6-one: S. A. Monti and S. Yuan, *J. Org. Chem.*, **36**, 3350 (1971).
(5) Formation of this diene does not interfere with the automerization. In particular, it does not provide a mechanism for mixing C_9 deuterons with C_7 protons, since heating a mixture of 80% C_9-undeuterated 3a and 20% of 6-trideuteriomethylbicyclo[3.2.1]octa-2,6-diene for three automerization half-lives gives recovered 6-methylenebicyclo[3.2.1]oct-2-ene with no deuterium at C_9.