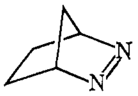
Table I. Photolysis at 366 mμ of 0.02 *M* 2,3-Diazabicycloheptene-2 at 20°

Sensitizer (concn, *M*)	E_T, kcal[4]	Solvent	k_1,[a] 10^{-3} sec^{-1}	Φ
Anthracene (0.053)	42.6[b]	Toluene	2.7	<0.00017
Pyrene (0.050)	48.7	Hexane	0.65	0.00029
β-Acetonaphthone (0.10)	59.3	Hexane	3.3	0.0079
Phenanthrene (0.10)	62.2	Hexane	9.0	0.0077
Phenanthrene (0.050)	62.2	Toluene	9.0	0.0054
Thioxanthone (0.052)	65.5	Toluene	13	1.0
Triphenylene (0.108)	66.6	Toluene	1.6	0.77[c]
Benzophenone (0.10)	68.5	Hexane	530[d]	0.97

[a] Experimental rate constant for decay of sensitizer triplet; see footnote *b*. [b] W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966). [c] Photolyzed at 313 mμ. [d] H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

compound of rigid structure would accomplish this end since changes in geometry concomitant with energy transfer would be highly unfavorable.[10] It was hoped that an azo group incorporated into a bicyclooctyl system would meet this requirement. Unfortunately, such a compound proved to be rather photostable, so the bicycloheptyl analog[12] I was used instead. We have obtained the quantum yields of nitrogen formation shown in Table I.



I

Although we cannot presently explain the difference within the two groups of sensitizers, the distinction between those of high and low energy is clear. A high quantum yield of nitrogen formation implies efficient triplet energy transfer since benzophenone and triphenylene are known to have high intersystem-crossing ratios,[13] and virtually all the light is absorbed by the sensitizer.

Since energy transfer is efficient only when the sensitizer is of higher energy than the acceptor,[8] the data indicate that the triplet compound I lies between 62.2 and 65.5 kcal. The singlet of I is at 84.4 kcal[1] so that the singlet–triplet splitting becomes 18.9–22.2 kcal. Although there is likely to be some influence of structure on E_{S-T}, our value is roughly in agreement with the estimated value.[5] The sensitizer decay constants listed in Table I show clearly that the observed break in quantum yield is not a function of sensitizer lifetime.

Results qualitatively similar to ours have been noted by Andrews and Day,[14] who used various sensitizers and an alkylidenepyrazoline. Their cutoff was apparently less well defined than ours but occurred in the region 55–65 kcal.

It would be interesting to measure energy transfer rates to rigid and nonrigid azo compounds using kinetic spectroscopy as has been elegantly done by Hammond and co-workers[15] for stilbenes. Such experiments could lend a great deal of support to the arguments given above.

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[10] Two types of geometrical changes which might occur in an acyclic azo compound but not in a rigid system are twisting about the N=N bond[5b] and straightening of one or two C–N bonds in the molecular plane.[11] In support of the idea that one of these processes does occur, we mention that we have observed efficient photosensitized *trans-cis* isomerization of azomethane.

[11] J. Alster and L. Burnelle, *J. Am. Chem. Soc.*, **89**, 1261 (1967).

[12] S. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961).

[13] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Inc., New York, N. Y., p 131.

[14] S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

[15] See footnote *b*, Table I.

Paul S. Engel
Converse Memorial Laboratory, Harvard University
Cambridge, Massachusetts 02138

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Heterocyclic Metallo-Indene Systems

Sir:

The preparation of five-membered unsaturated organometallic heterocycles and spirocycles through the reaction of a 1,4-dilithium system and a metallic or pseudo-metallic halide has received extensive attention in the literature. This type of reaction has produced a host of novel metallocyclopentadienes[1–4] when 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, originally described by Smith and Hoehn,[5] was the reactive organometallic intermediate employed. Similarly, metallofluorenes[6,7] and perfluorinated analogs[8] have been prepared by the reactions of the respective 2,2′-dilithiobiphenyl systems. Thus far this particular type of reaction has not been exploited for the synthesis of metallo-indenyl counterparts of the above heterocycles, although three such compounds are known. These have been prepared by specific reactions of diphenylacetylene with $Fe_3(CO)_{12}$ to give a ferraindene complex,[9] with triphenylaluminum to give an aluminole,[10] and with selenium tetrachloride to give a selenium heterocycle.[11]

The reaction of diphenylacetylene with *n*-butyllithium produces a dilithium intermediate (I) which has been previously characterized by the carbonation studies of Mulvaney, *et al.*[12] This reagent appeared to offer a facile entry into such metallo-indenyl derivatives. We have developed improved techniques for the generation of I and herein report our initial successful results on the subsequent reactions of I to afford a variety of heterocyclic and spirocyclic metallo-indenyl systems.

The reaction of diphenylacetylene with *n*-butyllithium in 1:1 diethyl ether–tetrahydrofuran (THF)

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(1) F. C. Leavitt, T. A. Manuel, and F. Johnson, *J. Am. Chem. Soc.*, **81**, 3163 (1959); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

(2) K. Rühlmann, *Z. Chem.*, **5**, 354 (1965).

(3) M. D. Curtis, *J. Am. Chem. Soc.*, **89**, 4241 (1967).

(4) E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961).

(5) L. I. Smith and H. H. Hoehn, *ibid.*, **63**, 1184 (1941).

(6) H. Gilman and R. D. Gorsich, *ibid.*, **80**, 1883 (1958).

(7) R. Gelius, *Chem. Ber.*, **93**, 1759 (1960).

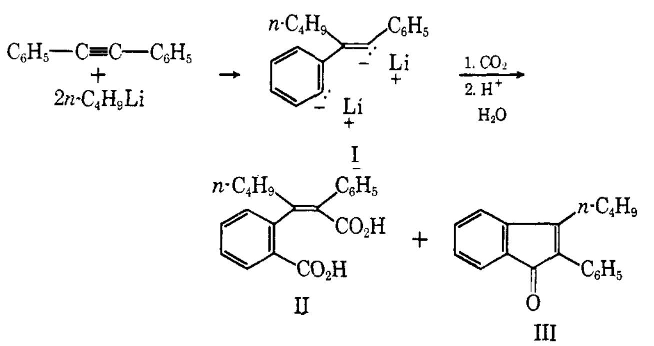
(8) S. C. Cohen and A. G. Massey, *Chem. Commun.*, 457 (1966); S. C. Cohen and A. G. Massey, *Tetrahedron Letters*, 4393 (1966).

(9) E. H. Braye and W. Hübel, *J. Organometal. Chem.* (Amsterdam), **3**, 38 (1965).

(10) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2976 (1966).

(11) R. F. Riley, J. Flato, and P. McIntyre, *J. Org. Chem.*, **28**, 1138 (1963).

(12) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton, *ibid.*, **88**, 476 (1966).



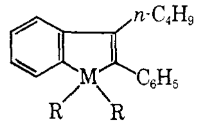
or with N,N,N′,N′-tetramethylethylenediamine (TMEDA) complexed n-butyllithium in hexane[13] produces I in yields higher than those obtained when the reaction is carried out in diethyl ether alone.[12] I was characterized by carbonation over Dry Ice, and the yield data are summarized in Table I.

Table I. Yield Data (%) for Formation of I as Determined by Carbonation

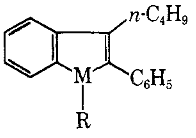
Product	1:1 Et_2O-THF system	TMEDA-hexane system	Et_2O system
II	27	30	14[a]
III	11[b]	17[b]	16[a,c]

[a] See ref 12. [b] Yield determined by isolation of 2,4-dinitrophenylhydrazone derivative from the neutral fraction of the reaction mixture. [c] Yield determined by vapor-phase chromatography of the neutral fraction.

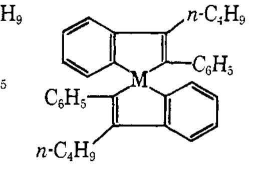
Preparation of I in 1:1 ether-THF or in TMEDA-hexane and subsequent reaction with diphenyldichlorosilane in refluxing THF produces, after chromatography on alumina, 3-n-butyl-1,1,2-triphenyl-1-silaindene[14] (IV) in yields of 46 and 55%, respectively. After recrystallization from methylene chloride-methanol, IV was obtained in the form of colorless platelets, mp 84–84.5°. *Anal.* Calcd for $C_{30}H_{28}Si$: C, 86.48; H, 6.78; Si, 6.74; mol wt, 417. Found: C, 86.15; H, 7.14; Si, 6.63; mol wt,[15] 413. An nmr spectrum[16] of this compound exhibited resonances for aromatic protons at τ 2.56 (multiplet, 19 H's) and for aliphatic protons at τ 7.30, 8.55, and 9.12 (broadened multiplets, 9 H's).



IV, M = Si;
R = C_6H_5
VII, M = Sn;
R = -CH=CH_2



V, M = P;
R = C_6H_5
VI, M = P(O);
R = C_6H_5



VIII, M = Sn
IX, M = Ge
X, M = Si

Reaction of I with dichlorophenylphosphine afforded 3-n-butyl-1,2-diphenylbenzophosphole (V) as colorless plates, mp 90–91.2°, in 40% yield. *Anal.* Calcd for $C_{24}H_{23}P$: C, 84.18; H, 6.77; P, 9.05; mol wt, 342. Found: C, 83.85; H, 6.79; P, 9.08; mol wt,[15] 353. The corresponding phosphole oxide (VI) was prepared in 90% yield by the peroxide oxidation of V.

The product formed on reaction of I with divinyltin dichloride was not the expected divinyltin heterocycle (VII). The only insolable product, obtained in 9% yield, was shown to be pure by thin layer chromatography (tlc) experiments and had a melting point of 139.5–140.5°. Its nmr spectrum had an integrated aromatic to aliphatic proton ratio of 1.0, and a total analysis suggested a molecular formula of $C_{36}H_{36}Sn$. Evidence pointed toward the formation of the tin spirocycle VIII in this reaction, since nucleophilic displacements of vinyl groups from tin are known in the literature.[17] A compound assigned the spirocyclic structure VIII was subsequently prepared in 28% yield by the reaction of I with tin tetrachloride in ether solution. Its nmr and infrared spectra and tlc properties were in excellent agreement with those of the divinyltin dichloride reaction product. Recrystallization from methylene chloride-methanol afforded white crystals, mp 141.8–142.5°. *Anal.* Calcd for $C_{36}H_{36}Sn$: C, 73.61; H, 6.18; Sn, 20.21; mol wt, 587. Found: C, 73.85; H, 6.16; Sn, 20.02; mol wt,[15] 583.

Substitution of germanium tetrachloride or silicon tetrachloride for the source of the spiro atom has likewise given the crystalline spirocycles IX and X in yields of 28 and 22%, respectively. Analytical data together with molecular weight determinations and nmr spectra confirmed the structures of these compounds.

We are presently studying the reactions of I and related 1,4-dilithium intermediates with various transition metal halides. The details of this work and reactions of metallo-indenyl derivatives will be the subject of future publications.

Acknowledgment. The authors wish to thank the Metal and Thermit Co. and the Dow Corning Corp. for generous gifts of organotin and organosilicon intermediates used in this investigation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in partial support of this research.

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(13) M. D. Rausch and D. J. Ciappenelli, *J. Organometal. Chem.* (Amsterdam), **10**, 127 (1967).

(14) The guidance of Dr. Kurt L. Loening of the Chemical Abstracts Service for his suggestions on the nomenclature and numbering is gratefully acknowledged.

(15) Molecular weight determinations were run at 50° in benzene on a Mechrolab Model No. 302 osmometer.

(16) Recorded on a Varian A-60 nuclear magnetic resonance spectrometer in a saturated $CDCl_3$ solution.

(17) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(18) National Science Foundation Graduate Trainee, 1965–1967.

M. D. Rausch, L. P. Klemann[18]
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

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The Conservation of Oxidative Energy. Formation of Acyl Anhydrides *via* the Oxidation of Hydroquinone Monocarboxylic Esters

Sir:

The energy released in the course of oxidation of hydroquinone monoesters can be trapped and conserved in the form of highly reactive chemical species, such as acid anhydrides. The principle has been demonstrated by oxidation of the hydroquinone esters I and II in glacial acetic acid, whereupon acetic anhydride is formed from the hydroquinone monoacetate