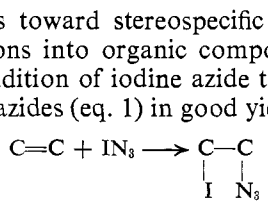
Table I

Olefin	Adduct[a]	Yield, %
Cyclohexene	*trans*-1-Azido-2-iodocyclohexane	82
Styrene	α-Azido-β-iodoethylbenzene	70
cis-Stilbene	*threo*-1-Azido-2-iodo-1,2-diphenylethane	63 (89–90°)[b]
trans-Stilbene	*erythro*-1-Azido-2-iodo-1,2-diphenylethane	80 (133–134°)
cis-2-Butene	*threo*-2-Azido-3-iodobutane	67
trans-2-Butene	*erythro*-2-Azido-3-iodobutane	64
2-Cholestene	2β-Azido-3α-iodocholestane	20 (101–102°)

[a] Satisfactory analyses were obtained for all new compounds. All spectral data (infrared n.m.r., mass) are consistent with the assigned structure. [b] The numbers in parentheses indicate melting points. All other compounds were obtained as liquids.

with our efforts toward stereospecific introduction of nitrogen functions into organic compounds,[3] we wish to report the addition of iodine azide to olefins leading to β-iodo alkyl azides (eq. 1) in good yield (see Table I).

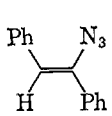


(1)

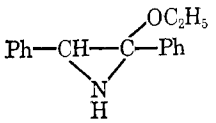
Iodine azide was described by Hantzsch[4] as an unstable solid prepared from silver azide and iodine. We were able to generate this pseudohalogen more conveniently from iodine monochloride and sodium azide in dimethylformamide or acetonitrile solution and add it *in situ* to several olefins.[5] That this addition occurs stereospecifically *trans* is shown by exclusive formation of the *threo*- and *erythro*-2-azido-3-iodobutane, respectively, from *cis*- and *trans*-2-butene. Similar stereospecificity was observed for *cis*- and *trans*-stilbene. Furthermore the product of addition to 2-cholestene is the *trans*-diaxial 2β-azido-3-α-iodocholestane.[6] Addition of iodine azide to styrene followed by subsequent dehydrohalogenation yielded the known α-azido styrene[7] thereby establishing the position of the azide function. These data are accommodated by assuming an iodonium ion intermediate which is opened *trans*-diaxially in the steroid example and at the benzylic carbon in the styrene case[8] by the azide ion.

trans-1-Azido-2-iodocyclohexane on dehydrohalogenation with base yields only 3-azidocyclohexene, suggesting the low acidity of a hydrogen α to an azide function.

Reaction of *threo*-1-azido-2-iodo-1,2-diphenylethane with alcoholic base yields α-azido-*trans*-stilbene (I), m.p. 43–45°. Light irradiation of I might be expected to lead to 2-phenylindole *via* a nitrene intermediate in



I



II

(3) A. Hassner and C. Heathcock, *J. Org. Chem.*, **30**, 1748 (1965).
(4) A. Hantzsch, *Ber.*, **33**, 524 (1900).
(5) The same products are obtained if olefin is added to a clear orange solution obtained by filtration of the sodium azide–iodine monochloride reaction mixture. This infers that one is dealing with an iodine azide species in solution. A mixture of bromine and sodium azide leads merely to the formation of dibromide from the olefin.
(6) For conformation assignments in steroids based on n.m.r. spectra see A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).
(7) G. Smolinsky, *ibid.*, 27, 3557 (1962).
(8) A. Hassner and C. Heathcock, *Tetrahedron Letters*, 1125 (1964).

analogy with the suggestion by Wenkert and Barnett[9] for the pyrolysis of 2-phenylcyclohexanone oxime to tetrahydrocarbazole. However, the only product, isolated in 40% yield from the photolysis of I in cyclohexane, was 2,3,5,6-tetraphenylpyrazine. This product may have arisen from the initially formed 2,3-diphenylazirine. On the other hand, treatment of *erythro*-1-azido-2-iodo-1,2-diphenylethane with ethanolic base yielded only 2,3-diphenyl-2-ethoxyaziridine (II), m.p. 83–85°, and no unsaturated azide. The structure of II was obvious from its n.m.r. and mass spectrum and from its conversion under acid conditions to 2,3,5,6-tetraphenylpyrazine.[10]

Reduction of the azido function in β-iodo azides can be accomplished by means of diborane. Thus α-azido-β-iodoethylbenzene was converted to α-amino-β-iodoethylbenzene in 75% yield, isolated as its hydrochloride.

(9) E. Wenkert and B. F. Barnett, *J. Am. Chem. Soc.*, **82**, 4671 (1960).
(10) α-Amino ketones are known to dimerize readily and ultimately to lead to pyrazines.

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An Electron Impact Study of the Bond Dissociation Energies of Some Trimethyltin Compounds

Sir:

In common with many areas of organometallic chemistry, bond dissociation energies in organotin compounds are virtually unknown. However, a considerable body of thermochemical data is available for alkyltin molecules,[1–7] which combined with electron impact dissociation data permits calculation of bond dissociation energies in these compounds. We wish to report here results of such an electron impact study of the formation of the trimethylstannium ion from substituted trimethylstannanes.

Appearance potentials of the $(CH_3)_3Sn^+$ ion were determined by the retarding potential difference method[8] on a modified Bendix Model 14-101 time-of-flight mass spectrometer. The energy spread of the electrons was approximately 0.1 e.v. and xenon was used to calibrate the electron energy scale. The results are shown in Table I. The indicated uncertainties in the appearance potentials are average deviations for replicate experiments performed over a period of several months.

The appearance potentials in Table I were measured for *m/e* 165 which corresponds to the Sn^{120} isotope and which is the most abundant mass peak in all the spectra. The agreement of our appearance potential

(1) E. R. Lippincott and M. C. Tobin, *J. Am. Chem. Soc.*, **75**, 4141 (1953).
(2) W. J. Jones, D. P. Evans, T. Gulwell, and D. C. Griffith, *J. Chem. Soc.*, 39 (1935).
(3) W. F. Lautsch, *Chem. Tech.* (Berlin), **10**, 419 (1958).
(4) A. A. Balandin, E. I. Klabunovskii, M. P. Kozina, and O. D. Ul'yanova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 12 (1957).
(5) C. R. Dillard, E. H. McNeill, D. E. Simmons, and J. B. Yeldell, *J. Am. Chem. Soc.*, **80**, 3607 (1958).
(6) I. B. Rabinovich, V. I. Telnoi, P. N. Nikolhev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **138**, 852 (1961).
(7) J. V. Davies, A. E. Pope, and H. A. Skinner, *Trans. Faraday Soc.*, **59**, 2237 (1963).
(8) R. E. Fox, W. M. Hickam, and T. Kjeldaas, *Rev. Sci. Instr.*, **26**, 1101 (1955).

Table I. Appearance Potentials of the $(CH_3)_3Sn^+$ Ion from Some $(CH_3)_3SnX$ Compounds

X	A.P., e.v.	$\Delta H_f°$, kcal. mole^{-1} $(CH_3)_3SnX$	$(CH_3)_3Sn^+$
CH_3	9.72 ± 0.06	−4.6[a]	186 ± 2
C_2H_5	9.47 ± 0.15	−7.1[a]	186 ± 4
n-C_3H_7	9.50 ± 0.12	−11.6[b]	187 ± 4
$Sn(CH_3)_3$	9.84 ± 0.09	−5.4[a]	35 ± 4[c]

[a] Reference 7. [b] Calculated by the method described in ref. 7. [c] $\Delta H_f°$ of the $(CH_3)_3Sn$ radical.

of the trimethylstannium from $(CH_3)_4Sn^{120}$ with that of Hobrock and Kiser[9] from $(CH_3)_4Sn^{116}$ (9.9 ± 0.15), and the similarity of the relative intensities of the isotopic $(CH_3)_3Sn^+$ species from all the molecular sources with the isotopic abundances of the tin isotopes, leads us to conclude that interference from carbon–hydrogen bond rupture is not significant. This would be especially true near the low threshold values observed. The heats of formation of the trimethylstannium ion were calculated from the appearance potentials and the assumption that we are observing the simple dissociation process (eq. 1) involving no excess

$$(CH_3)_3SnX + e \longrightarrow (CH_3)_3Sn^+ + X + 2e \qquad (1)$$

energy. The agreement of the ionic heats of formation from the three molecular sources supports this assumption and attests to the precision of the data. Combining the heat of formation of the trimethylstannium ion with the appearance potential from hexamethyldistannane, and again assuming no excess energy, leads to the value shown in Table I for the heat of formation of the trimethylstannyl radical. These data can then be combined to give a value of 6.54 e.v. for the ionization potential of the trimethylstannyl radical.

Taking the heat of formation of $(CH_3)_3Sn$ from Table I and the molecular heats of formation of trimethylstannane derivatives from Davies, Pope, and Skinner,[7] we arrive at the bond dissociation energies shown in Table II. In computing these dissociation energies we have used the following radical heats of formation: $\Delta H_f°(CH_3) = 33 \pm 1$,[10,11] $\Delta H_f°(C_2H_5) = 25.5 \pm 2$,[10,11] $\Delta H_f°(C_3H_7) = 20.5 \pm 2$,[12] $\Delta H_f°(C_6H_5) = 72 \pm 2$,[13] $\Delta H_f°(C_6H_5CH_2) = 42 \pm 3$,[14] $\Delta H_f°(C_2H_3) = 65 \pm 3$.[15] The bond dissociation energies are compared in Table II to the average bond energy values derived from the molecular heats of formation and heats of atomization. It is obvious that the average bond energies reflect very poorly the actual bond dissociation energies in the trimethylstannane derivatives and therefore very little reliance should be placed on the average bond energies in reaction mechanism considerations. However, the rather remarkably constant difference of 20–21 kcal. mole^{-1} between D and E as shown in the last column of Table II provides a means of correcting average bond energies. If $D - E$ be viewed as an energy of "reorganization" of the $(CH_3)_3Sn\cdot$ radical, which occurs on rupture of the $(CH_3)_3Sn$–X bond,[16] then on rupture of the $(CH_3)_3Sn$–$Sn(CH_3)_3$ bond this "reorganization" must occur twice. This will, of course, lead to a doubling of $D - E$ as is borne out in the last column of Table II.

(9) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **65**, 2186 (1961).
(10) G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961).
(11) B. E. Knox and H. B. Palmer, *Chem. Rev.*, **61**, 247 (1961).
(12) J. A. Kerr and J. G. Calvert, *J. Am. Chem. Soc.*, **83**, 3391 (1961).
(13) W. Fielding and H. O. Pritchard, *J. Phys. Chem.*, **66**, 821 (1962).
(14) A. H. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 439 (1957).
(15) A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 519 (1960).

Table II. Bond Dissociation Energies in Some Trimethylstannane Derivatives

Bond	D, kcal. mole^{-1}	$\bar{E}$,[a] kcal. mole^{-1}	$D - \bar{E}$, kcal. mole^{-1}
$(CH_3)_3Sn$–CH_3	73 ± 4	52	21
$(CH_3)_3Sn$–C_2H_5	68 ± 4	48	20
$(CH_3Sn$–n-$C_3H_7)$	68 ± 6	48	20
$(CH_3)_3Sn$–Br	94 ± 4	74	20
$(CH_3)_3Sn$–I	80 ± 4	59	21
$(CH_3)_3Sn$–C_3H_5	81 ± 5	61	20
$(CH_3)_3Sn$–$CH_2C_6H_5$	57 ± 5	36	21
$(CH_3)_3Sn$–C_2H_3	78 ± 5	57	21
$(CH_3)_3Sn$–$Sn(CH_3)_3$	76 ± 6	35	41

[a] Reference 1.

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(16) We are grateful to Dr. H. A. Skinner for this interpretation.

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Photochemical Transformations of a β,γ-Epoxy Ketone[1]

Sir:

The light-induced α,β-epoxy ketone rearrangement to the corresponding 1,3-diketone was studied as early as 1918[2] and has been re-explored extensively in recent years.[3] The photoisomerization has been described by two consecutive steps: a cleavage of the C_α-O bond of the oxide ring followed by a 1,2-shift of the β-hydrogen to the α position.[3b] The driving force for the fission of the epoxide ring was attributed to the tendency of the excited n–π* state to eliminate α substituents as odd electron or anionic species according to the reaction medium.[3b] In contrast to the exhaustive studies concerned with the photochemistry of α,β-epoxy ketones there has been no attempt, to date, to examine the phototransformations of the related β,γ-acyl oxide system. We now wish to demonstrate that, although a formally analogous rearrangement occurs,

(1) Photochemical Transformations of Small Ring Carbonyl Compounds, part V. For Part IV, see A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **87**, 1821 (1965).
(2) S. Bodforss, *Chem. Ber.*, **51**, 214 (1918).
(3) (a) C. K. Johnson, B. Dominy, and W. Reusch, *J. Am. Chem. Soc.*, **85**, 3894 (1963); (b) H. E. Zimmerman, R. B. Cowley, C. Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964); (c) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964); (d) E. F. Ullman, *J. Am. Chem. Soc.*, **85**, 3529 (1963); (e) J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964); (f) H. E. Zimmerman and R. D. Simkin, *ibid.*, 1847 (1964).