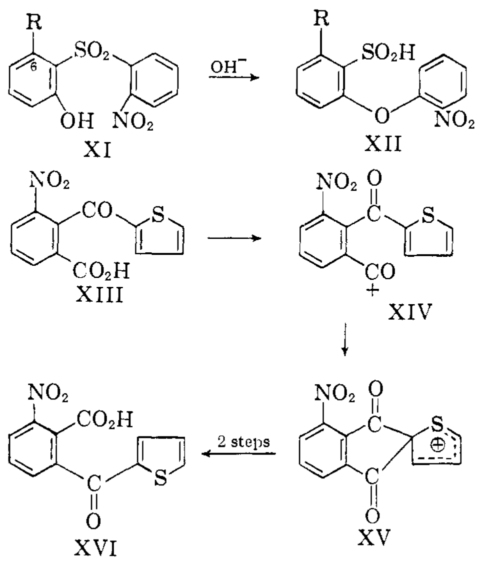


pseudo methyl ester (in addition to 65% of the normal ester). The formation of pseudo ester under acid-catalyzed esterification conditions probably occurs by a mechanism which involves primary attack at the ketonic carbonyl.[11] Thus, both esterification of this ketoacid and alkaline hydrolysis of its normal ester probably proceed by initial attack on the ketonic carbonyl group.

The reasons for measuring the rates of alkaline hydrolysis of various alkyl acetates have been stated.[12] In Table II are listed the rates of hydrolysis of other secondary alkyl acetates, together with certain rates previously determined. Probably the main point of interest is the fact that several of the secondary alkyl acetates hydrolyze at rates considerably slower than that of *t*-butyl acetate.

In conclusion, the authors would like to thank Drs. H. Shechter and W. N. White for interesting discussions concerning mechanisms of alkaline hydrolysis.

TABLE II

ALKALINE HYDROLYSIS OF ALKYL ACETATES IN 70% DIOXANE-WATER

R in CH_3COOR	$\dfrac{k_{30^0}\ (CH_3COOCH(CH_3)_2)^a}{k_{30^0}\ (CH_3COOR)}$
CH_3CHCH_3	1.0[b]
$CH_3CHCH_2CH_3$	2.2
$CH_3CH_2CHCH_2CH_3$	3.9
$CH_3CHCH(CH_3)_2$	5.8[c]
$CH_3CH_2CHCH(CH_3)_2$	12.1[d]
$CH_3CHC(CH_3)_3$	13.0[d]
$[(CH_3)_2CHCH_2]_2CH-$	21.6[d]
$CH_3CH_2CHC(CH_3)_3$	135
$(CH_3)_2CHCHCH(CH_3)_2$	151
$(CH_3)_2CHCHC(CH_3)_3$	151
$(CH_3)_3CCHC(CH_3)_3$	200
$(CH_3)_3C-$	15.1[d]

[a] The rates of alkaline hydrolysis were determined essentially as described; all esters were essentially pure as determined by vapor phase chromatography. [b] The rate determined in the present work for isopropyl acetate as standard, 10^3k, l./mole/sec., 12.1, was very close to that, 10^3k, l./mole/sec., 12.4, determined previously.[2] [c] The relative rate for this compound determined in the present work did not agree with that (2.4) determined previously[13]; we believe the present value to be correct. [d] These values are calculated from rate constants reported previously.

Experimental

The rate constant determinations were carried out essentially as described.[12] The esters of the substituted *o*-benzoylbenzoic acids had the physical constant reported.[11,13] The alkyl acetates used were all homogeneous as judged by vapor phase chromatographic analysis. The rate constants reported in Tables I and II are the average of at least two determinations.

---

(11) See M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941). The addition product shown in brackets for the first step would, according to more modern concepts, go to a carbonium ion which, by intramolecular attack on the oxygen (an attack on either oxygen could be rationalized) of the carbonyl group, would lead to the pseudo ester.

(12) S. Sarel, L. Tsai and M. S. Newman, *ibid.*, **78**, 5420 (1956).

(13) M. S. Newman and B. T. Lord, *ibid.*, **66**, 731 (1944).

COMMUNICATIONS TO THE EDITOR

REDUCTION OF ALKYL HALIDES BY ORGANOTIN HYDRIDES. EVIDENCE FOR A FREE RADICAL MECHANISM[1]

Sir:

It has been shown that organotin hydrides are capable of bringing about replacement of the halogen in alkyl,[2,3] aryl,[2,4] and acyl[5] halides by hydrogen. We have extended the fragmentary observations on the reduction of alkyl halides to include examination of the scope and mechanism of reaction (1).

$$(4 - n)RX + R'_nSnH_{4-n} \longrightarrow (4 - n)RH + R'_nSnX_{4-n} \quad (1)$$

---

(1) This research was supported by the National Science Foundation under grant NSF-G-10,000.

(2) J. G. Noltes and G. J. M. van der Kerk, *Chem. and Ind.*, 294 (1959).

(3) E. J. Kupchik and R. E. Connolly, *J. Org. Chem.*, **26**, 4747 (1961).

(4) L. A. Rothman and E. I. Becker, *ibid.*, **24**, 294 (1959); **25**, 2203 (1960).

(5) H. G. Kuivila, *ibid.*, **25**, 284 (1960).

TABLE I

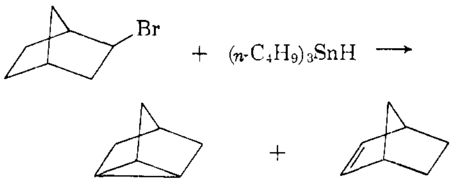
REDUCTION OF ORGANIC HALIDES BY ORGANOTIN HYDRIDES

Item	Tin hydride	Halide	Conditions[a]	% Yield[b]	
				Reduction product	Organotin halide
1	$(n\text{-}C_4H_9)_3SnH$	$C_6H_5CH_2Br$	4 *M* in ether, ex., 12 hr.	68	91
2	$(n\text{-}C_4H_9)_3SnH$	$C_6H_5CH_2Cl$	Neat, 150°, 20 min.	78	80
3	$(n\text{-}C_4H_9)_3SnH$	Cyclo-$C_6H_{12}Br$	Neat, ex., 1 hr.	71	94
4	$(n\text{-}C_4H_9)_3SnH$	Cyclo-$C_6H_{12}Cl$	Neat, 120°, 40 min., inc. rxn.	36	*d*
5	$(n\text{-}C_4H_9)_3SnH$	$n\text{-}C_8H_{17}Br$	Neat, ex., 1 hr.	80	90
6	$(n\text{-}C_4H_9)_3SnH$	$C_6H_{13}CHBrCH_3$	Neat, ex., 1 hr.	78	92
7	$(n\text{-}C_4H_9)_3SnH$	$C_6H_5CHClCH_3$	Neat, 100°, 17 hr.	77	90
8	$(C_6H_5)_3SnH$	$C_6H_5CHClCH_3$	Neat, ex., 18 hr.	89	86
9	$(C_6H_5)_3SnH$	Cyclo-$C_3H_5CH_2Cl$	Neat, 130°, 5 hr.	No reaction	
10	$(C_6H_5)_3SnH$	$CH_2CH{=}CHCH_2Cl$	Neat, ambient temp., 18 days	*c*	*d*
11	$(C_6H_5)_3SnH$	$CH_3CHClCH{=}CH_2$	Neat, ambient temp., 18 days	*c*	*d*
12	$(C_6H_5)_3SnD$	$(+)C_6H_5CHClCH_3$	Neat, ambient temp., 72 hr.	57[e]	*d*
13	$(n\text{-}C_4H_9)_3SnH$	$C_6H_5COCH_2Br$	4 *M* in C_6H_6, 12 hr.	84[f]	96
14	$(n\text{-}C_4H_9)_3SnH$	$C_6H_5COCH_2Cl$	Neat, 150°, 45 min.	71[f]	82
15	$(n\text{-}C_4H_9)_3SnH$	3-Bromocamphor	4 *M* in ether, ex., 2 hr.	61[f]	*d*
16	$(n\text{-}C_4H_9)_3SnH$	*meso*-$(C_6H_5CHBr)_2$	Neat, 100°, 15 hr.	85[g]	*d*
17	$(n\text{-}C_4H_9)_2SnH_2$	$C_6H_5CH_2Cl$	Neat, ex., 12 hr.	83	96

[a] Ex., reactants mixed at room temperature, exothermic reaction; temp. allowed to rise no higher than 50°. [b] Isolated products, infrared spectra compared with those of authentic samples. [c] Mixture of 1- and 2-butenes, products from items 10 and 11 identical. [d] Not isolated. [e] Racemic $C_6H_5CHDCH_3$. [f] Product unhalogenated ketone only, no alcohol. [g] *trans*-Stilbene, 92% of theoretical H_2 collected.

Salient results are presented in Table I. Comparison of items 1 *vs*. 2, 3 *vs*. 4, 6 *vs*. 7, and 13 *vs*. 14, shows clearly that bromides are reduced more readily than the corresponding chlorides. As indicated by items 13, 14, and 15, α-haloketones are selectively and cleanly reduced to the corresponding unhalogenated ketones, the absence of alcohols being shown by infrared spectra of the products. Vicinal dihalides undergo elimination as exemplified (item 16) by the conversion of *meso*-stilbene dibromide to *trans*-stilbene. Geminal dihalides undergo normal reduction. A case in point is the stepwise conversion of benzotrichloride to benzal chloride, to benzyl chloride, and to toluene in good yields by tri-*n*-butyltin hydride (not shown in the table).[6] Comparison of items 2 and 17 shows that di-*n*-butyltin dihydride is more effective than tri-*n*-butyltin hydride; items 7 and 8 indicate that triphenyltin hydride is superior to tri-*n*-butyltin hydride. Infrared spectra of products indicate the absence of olefins in the reduction products.

Evidence that the reaction involves the formation of either free radicals or carbonium ions is provided by the following observations. Optically active α-phenylethyl chloride, upon reduction with triphenyltin deuteride, gives racemic α-deuteriophenylethane under conditions which do not cause the racemization of the chloride. When α- and γ-methylallyl chlorides are reduced, they give identical (according to infrared spectra) mixtures of 1- and 2-butenes, under conditions which do not cause isomerization of the chlorides. Propargyl bromide, upon reduction with tri-*n*-butyltin hydride, yields a mixture of propyne and allene. Finally, 2-bromonortricyclene yields a mixture of norbornene and nortricyclene (reaction 2).



(2)

Evidence that free radicals rather than carbonium ions are involved is provided by the fact that cyclopropylcarbinyl chloride (item 9) is resistant to reduction whereas the isomeric methylallyl chlorides (items 10 and 11) are reduced readily at room temperature by triphenyltin hydride. This order of reactivity is opposite to that observed in the solvolyses of cyclopropylcarbinyl and allyl halides in aqueous ethanol.[7] Further evidence is provided by the relative reactivity data presented in Table II.

TABLE II

RELATIVE RATE CONSTANTS FOR HALOGEN ATOM ABSTRACTION

R	Methyl radical[a]		Tin hydride reduction[b]
	I	Br	Br
C_2H_5	180		
$n\text{-}C_4H_9$			1
$s\text{-}C_3H_7$	870		
$s\text{-}C_4H_9$			2.99
$t\text{-}C_4H_9$	1680		7 ± 1
CH_2Cl		1.4	25.8 ± 0.3
$C_6H_5CH_2$		6.5	33.5 ± 0.3
$CHCl_2$		131	117 ± 3

[a] Relative rate constants for reactions $RX + CH_3\cdot \rightarrow R\cdot + CH_3X$ (k_2) expressed as a ratio k_2/k_1, where k_1 refers to the reaction $CH_3\cdot + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2\cdot$[8] [b] $RX + (n\text{-}C_4H_9)_3SnH \rightarrow RH + (n\text{-}C_4H_9)_3SnX$.

These were obtained by carrying out competitive reductions of the halides in the presence of insufficient tri-*n*-butyltin hydride at 45°. Included in the table are data obtained by Szwarc and co-workers[8]

---

(6) Analogous stepwise reduction starting from carbon tetrachloride has been observed by D. H. Lorenz and E. I. Becker, private communication.

(7) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(8) F. W. Evans, R. J. Fox and M. Szwarc, *ibid.*, **82**, 6414 (1960).

for the relative rates of abstraction of halogen atoms from alkyl halides by methyl radicals. These reactivities are closely parallel to each other, and different from those for SN1 reactions. One example is provided by the fact that benzyl bromide is more reactive than *t*-butyl bromide in the reduction, whereas *t*-butyl chloride solvolyses faster than benzyl chloride by a factor which depends strongly on the solvent.[9] The high reactivity of carbon tetrachloride (72.4), comparable to benzyl bromide (33.5), constitutes another.

The reactivity sequence bromide < iodide is shown by the fact that *n*-heptyl iodide is more reactive than *n*-butyl bromide by a factor of 65.

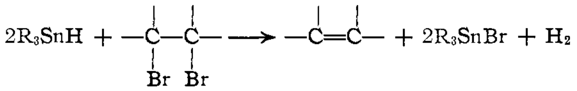
The data presented here are consistent with a mechanism in which the rate of formation of an alkyl free radical is the prime factor in determining reactivity of a halide. This might involve a chain mechanism in which an organotin radical abstracts a halogen atom from the halide in one step, and the resulting alkyl radical abstracts a hydrogen atom from the organotin hydride in the other step.[10]

Catalysis of the reaction by azobisisobutyronitrile confirms the existence of a chain mechanism: tri-*n*-butyltin hydride in toluene at 80 ± 2° reduced benzyl chloride, chlorocyclohexane, and bromobenzene to the extents of 100, 70, and 41% in 35 min. in the presence of 1.5 mole % of the catalyst, and to the extents of 26, 1, and 5% in its absence.

---

[9] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 616 (1956).

[10] This last statement cannot, of course, apply to the dehalogenation of vicinal dihalides, which proceeds according to the equation



$$2R_3SnH + -\underset{Br}{\overset{|}{C}}-\underset{Br}{\overset{|}{C}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- + 2R_3SnBr + H_2$$

[11] National Science Foundation Senior Postdoctoral Fellow, California Institute of Technology, 1959–1960.

DEPARTMENT OF CHEMISTRY HENRY G. KUIVILA[11]
UNIVERSITY OF NEW HAMPSHIRE
CONTRIBUTION NO. 2855 LAWRENCE W. MENAPACE
GATES AND CRELLIN LABORATORIES CHARLES R. WARNER
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

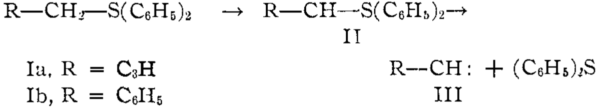
RECEIVED AUGUST 2, 1962

THE DECOMPOSITION OF SULFUR YLIDS TO CARBENES[1]

Sir:

Franzen and co-workers[2] recently studied the reaction of alkyldiphenyl-sulfonium salts with strong bases. On the basis of isolating triphenylmethane (42%), 1,1,1-triphenylpentane (15%) and 1-butene (7%) from the reaction of tritylsodium with *n*-butyldiphenylsulfonium tetrafluoroborate (Ia) they postulated that this salt was first converted to the corresponding ylid (IIa) (by proton abstraction) which then decomposed to phenyl sulfide and the carbene (IIIa). Similar results were reported for the benzyldiphenylsulfonium salt (Ib), affording 1,1,1,2-tetraphenylethane by an insertion reaction of the carbene (IIIb) with triphenylmethane. However, all attempts to trap the carbene intermediates with cyclohexene were unsuccessful. In fact, none of their products[3] require the postulation of carbenes as reaction intermediates. They can be accounted for by displacement and/or elimination reactions.

In our original work[1] on the chemistry of dimethylsulfoniumfluorenylide we obtained several products which were best accounted for by the ylid first decomposing to a carbene. We have now succeeded in demonstrating conclusively that sulfur ylids can be decomposed to carbenes by trapping the carbene formed from the ylid (IIb). Franzen and Wittig[4] previously reported the decomposition of trimethylammoniummethylide to methylene which was trapped with cyclohexene to form norcarane.



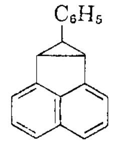
$$R-CH_2-\overset{+}{S}(C_6H_5)_2 \rightarrow \underset{\text{II}}{R-\overset{-}{C}H-\overset{+}{S}(C_6H_5)_2} \rightarrow$$

Ia, R = C_3H
Ib, R = C_6H_5

$$\underset{\text{III}}{R-CH:} + (C_6H_5)_2S$$

Addition of 4 mmoles of *n*-butyllithium solution to a slurry of 4.0 mmoles each of benzyldiphenylsulfonium tetrafluoroborate (Ib) and acenaphthylene in anhydrous tetrahydrofuran at −40° afforded 4.0 mmoles of lithium tetrafluoroborate (100%); 3.3 mmoles of phenyl sulfide (83%), determined and identified by oxidation to phenylsulfone, m.p. 122.5–124.5 (lit.,[5] m.p. 124°); 1.1 mmoles of unreacted acenaphthylene; and 1.2 mmoles of 7-phenyl - 7H - 6b,7a - dihydrocycloprop[a]acenaphthylene (IV) (43% based on unreacted acenaphthylene, 31% based on Ib), m.p. 170° dec.

The adduct (IV) was identified by its inertness to cold permanganate or bromine; by its infrared spectrum (no olefinic absorption, λ_{max} 13.70 and 14.83 μ, characteristic of monosubstituted aryl); by its ultraviolet spectrum (λ_{max} 232 mμ (log ϵ 4.3), 296 (3.6), 310 (3.5) and 323 (3.1)); and by oxidation with chromic acid to benzoic acid (m.p. 120–121°) and naphthalene-1,8-dicarboxylic acid anhydride, m.p. 272.5–274° (lit.,[6] m.p. 274), identified by admixture melting point and infrared spectra comparison with an authentic sample.



IV

We have found that other alkyldiphenylsulfonium ylids can be decomposed to carbenes which can be trapped with acenaphthylene and other olefins. We have also noted that this decomposition can be avoided by working at even lower temperatures. This work is continuing and will be published in detail at a later date.

---

[1] This is paper VII of our series "The Chemistry of Ylids"; for paper VI see Johnson and LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

[2] V. Franzen, H. J. Schmidt and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

[3] An unspecified amount of a (β-phenylisopropyl)-ethyl ether resulting from an insertion reaction of (possibly) the benzyl carbene on ethyl ether was reported and identified by vapor phase chromatography analysis and infrared spectrum.

[4] V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

[5] O. Hinsberg, *Chem. Ber.*, **43**, 290 (1910).

[6] C. Graebe and E. Gfeller, *ibid.*, **25**, 652 (1925).