INTRAMOLECULAR CYCLOPROPANE FORMATION

FROM GEM-DIIODOALKANES AND ZINC-COPPER COUPLE

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The "Simmons-Smith" reagent, formed by reaction of
methylene iodide and zinc-copper couple in diethyl ether, has
been used extensively for synthesis of cyclopropane rings
from olefins since it adds a methylene group across double
bonds, but has not been observed to insert a methylene group
in carbon-hydrogen single bonds (1). We present evidence
here for intramolecular carbon-hydrogen insertion reactions
of compounds which are homologous to the "Simmons-Smith"
reagent prepared by reaction of 1,1-diiodopropane (I) or
1,1-diiodo-2-methylpropane (II) with zinc-copper couple.

The diiodides I and II were synthesized by titrating
benzene solutions of diazopropane and 2-methyldiazopropane (2)
with an excess of a solution of iodine in benzene. The
resulting solutions were washed with aqueous sodium bisulfite,
dried, and concentrated under vacuum yielding the diiodides
as yellow liquids. To our knowlege I and II have not been
reported. The n.m.r. spectrum of I was identical to the n.m.r.

spectrum of authentic 1,1-dichloropropane except for the
chemical shift of the $-CHI_2$ triplet to higher field.
Contamination of I by 8% benzene was determined from the
n.m.r. spectrum. No other spurious peaks were observed.
Anal. Calcd. for $C_3H_6I_2$ (I) (corr. for 8% C_6H_6 by n.m.r.):
I, 78.9. Found: I, 79.4. The yellow liquid II gave an
n.m.r. spectrum in agreement with the structure, but
benzene contamination (2%) and trace spurious peaks
probably due to rearranged diiodides or vinyl iodides were
observed (4). Anal. Calcd. for $C_4H_8I_2$ (II) (corr. for 2%
C_6H_6 by n.m.r.): I, 80.3. Found: I, 76.8.

Volatile products were formed after induction periods
ranging from 3 to 10 minutes when a sample of I or II
(10^{-3} mole) was stirred with an equivalent amount of zinc-
copper couple (5) in cyclohexene (1 ml.) - diethyl ether
(4 ml.) in the dark at room temperature. The products (6)
formed from 1,1-diiodopropane (I) were propylene, propane
and cyclopropane in the molar ratio 380:16:1; from 1,1-
diiodo-2-methylpropane (II), isobutene, isobutane, trans-2-
butene, cis-2-butene, and methylcyclopropane were formed in
the molar ratio 280:24:2:1:1. The ratios did not vary with
time and duplicate runs gave identical results within
analytical error. This and other data (vide infra) suggest
that the products arise from the same intermediate (8).

We suggest that cyclopropane and methylcyclopropane
are formed from the intermediate organo-zinc compounds IIIa
and IIIb respectively (in which X may be iodine or the
iodoalkyl group), by 1,3-hydride shifts to the zinc-bound

carbon (either simultaneous with or after migration of
the carbon-bound iodine to zinc) and elimination of I-Zn-X
with simultaneous ring closure. Fig. I indicates this
transformation by a completely concerted mechanism to show
the bonds being made and broken. The compounds IIIa and
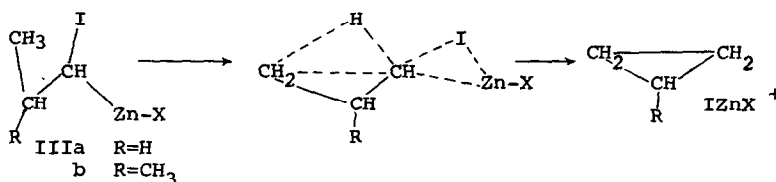IIIb are homologous to the

Fig. I

intermediates postulated by Blanchard, Simmons, and Smith for
the "Simmons-Smith" reagent (9, 10). If carbon-zinc cleavage
is simultaneous with the hydride shift, the cyclopropanes are
in fact formed by a carbon-hydrogen insertion reaction of a
I-Zn-X complexed carbene.

The olefin/cyclopropane ratios obtained in this study
were much larger than would be expected if "free" alkyl
carbenes (11) or alkyl carbonium ions (12) were intermediates
(unless two mechanistic pathways are invoked). If the
cyclopropanes arise by 1,3-hydride shifts the large steric
demand on the required transition state by the highly
solvated I-Zn-X group may explain the relatively high yields of
propylene or isobutene. The latter two compounds are formed
from IIIa and IIIb respectively by 1,2-hydride shifts analogous
to those postulated to explain olefin formation from reactions
of 1,1-diiodoethane and 2,2-diiodopropane with zinc-copper
couple (10). The 2-butenes may be formed from IIIb by 1,2-
methyl shifts.

The saturated hydrocarbons, propane, and isobutane, from IIIa and IIIb probably arise by a series of hydrolysis reactions of the intermediate organo-zinc compounds due to moisture contamination. Addition of water to the reaction mixture after formation of the volatile products gave rise to additional amounts of the acyclic saturated hydrocarbons (13), however the olefin/cyclopropane ratios remained unchanged strongly implying that the cyclopropanes did not arise by hydrolysis of cyclopropylzinc iodide or methylcyclopropylzinc iodide. Reaction of iodopropane with zinc-copper couple under our conditions did not give cyclopropane. Cyclopropanes were not formed in detectable amounts from I or II in the absence of zinc-copper couple.

Our data, however, do not rule out a series of 1,2-hydride shifts to give the cyclopropanes. Such a mechanistic ambiguity existed in the observation of cyclopropane formation from nitrous acid deamination of 1-aminopropane and "deoxideation" of 1-propanol (12,14,15). However it has been recently established that 1,2-hydride shifts are unimportant in these systems and the experimental data supports 1,3-hydride shifts (16,17). The I-Zn-X moiety is probably a good leaving group; this, coupled with the probable instability of the zwitterion which would be produced by one 1,-2-hydride shift, might be expected to favor simultaneous hydride shift and I-Zn-X elimination. Thus, all 1,2-hydride shifts would give olefin. We will test these hypotheses by comparing the propylene/cyclopropane ratios obtained in reaction of zinc-copper couple

with 1,1-diiodopropane-2,2-d$_2$ and the undeuterated com-

pound I. These studies will be extended to other metals

and geminal dihalides.

References

(1) H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 81,
     4256 (1959).

(2) Preparation of the diazo-compounds was accomplished
     analogously to a reported preparation of diazomethane
     beginning with the appropriate amines (3).

(3) F. Arndt, Org. Syntheses, Col. Vol. 2, pp. 165 and
     461, J. Wiley and Sons, Inc., New York, 1943.

(4) The compound II slowly decomposes even over copper
     wire in the dark in the refrigerator, whereas I
     is apparently quite stable under these conditions.
     The expected ease of hydrogen iodide elimination from
     II would explain this observation. Although we
     are not satisfied with the purity of II, and would
     not make mechanistic conclusions based solely on data
     obtained from it, we feel that the consistency in data
     obtained from I and II, and the apparent high purity of
     I lend credence to application of the mechanistic
     conclusions to the reactions (vide infra) of both
     I and II.

(5) R. S. Shank and H. :Shechter, J. Org. Chem., 24, 1825
     (1959).

(6) Analyzed by vapor phase chromatography on a 25' x 1/8"
     20% dimethylsulfolane (60/80 firebrick) column at 0°,
     40 p.s.i. nitrogen, 10 p.s.i. hydrogen, using a flame
     ionization detector. Identified by comparison of
     retention times with known samples of the hydrocarbons.
     In the case of reactions of II, a second calibrated
     column was also used which has been previously described
     (7).

(7) R. C. Neuman, Jr., ibid., In press.

(8) Trace amounts of other hydrocarbons have been detected
     and identified in all of these runs. Since it is not
     known at this time whether trace amounts of other diio-
     dides are present in I or II, no definite conclusions
     concerning these products can be made. The total
     yields of volatile hydrocarbons from I and II are 20% and

22% respectively based on the initial amount of diiodide.
The non-volatile products, which presumably (9,10) are
3-hexene and 2,5-dimethylhexene from I and II
respectively, have not been analyzed. The addition
reaction to double bonds is not expected with the
higher homologues of the "Simmons-Smith" reagent (10).
Analogous experiments in tetrahydrofuran as solvent
gave qualitatively the same results.

(9)   E.P. Blanchard and H. E. Simmons, J. Am. Chem. Soc., 86
      1337 (1964).

(10) H. E. Simmons, E. P. Blanchard, and R. D. Smith, ibid.,
      86, 1347 (1964).

(11) L. Friedman and H. Shechter, ibid., 81, 5512 (1959).

(12) P. S. Skell and I. Starer, ibid., 82, 2971 (1960).

(13) The hydrolysis reactions mentioned would be analogous
      to those producing methane from the "Simmons-Smith"
      reagent.'

(14) P. S. Skell and I. Starer, ibid., 84, 3962 (1962).

(15) P. S. Skell and R. J. Maxwell, ibid., 84, 3963 (1962).

(16) G. J. Karabatsos and C. E. Orzech, Jr., ibid., 84
      2838 (1962).

(17) A. A. Aboderin and R. L. Baird, ibid., 86, 2300
      (1964).