8 I. L. Ozanne and C. S. Marvel, *J. Am. Chem. Soc.*, 52 (1930) 5267.
9 H. G. Viehe, *Chem. Ber.*, 92 (1959) 3064.
10 C. Prévost, M. Gaudemar and J. Honigberg, *Compt. Rend.*, 230 (1950) 1186.
11 E. R. H. Jones, L. Skatteböl and M. C. Whiting, *J. Chem. Soc.*, (1956) 4765.
12 H. Buchert and W. Zeil, *Z. Physik. Chem. (Frankfurt)*, 29 (1961) 317.
13 L. H. Shchukovskaya and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1958) 1011; *Chem. Abstr.*, 53 (1959) 1119.
14 P. Mazerolles, *Bull. Soc. Chim. France*, (1960) 856
15 *Dictionary of Organic Compounds*, Eyre and Spottiswoode, London, 4th Edn., 1965, p. 1157.
16 Le Quan Minh, J. C. Billiotte and P. Cadiot, *Compt. Rend.*, 251 (1960) 730.
17 C. Eaborn, G. A. Skinner and D. R. M. Walton, *J. Chem. Soc.*, in the press.

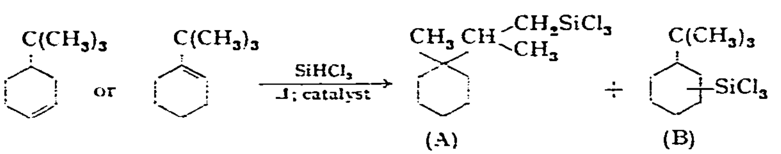
Received March 7th, 1966

PRELIMINARY NOTE

Skeletal rearrangements in the reaction of trichlorosilane with t-butylcyclohexenes

It is well established that when trichlorosilane is added to either internal or terminal olefins under catalysis by chloroplatinic acid, there is a marked tendency for the formation of a terminally substituted trichlorosilylalkane. Thus, both 1- and 2-pentene add trichlorosilane in the presence of chloroplatinic acid to form n-amyltrichlorosilane almost exclusively[1].

Since it has been shown[1] that the trichlorosilyl group does not migrate under the reaction conditions, it is believed that the olefin substrate must undergo isomerization to a terminal alkene before introduction of the silane. While various cyclic and acyclic olefins have been shown[2–6] to undergo double bond migration during the process of adding trichlorosilane, no evidence of skeletal rearrangements accompanying the formation of a terminally substituted product from an internal olefin (or *vice versa*) has been reported. We are hereby reporting just such an isomerization phenomenon involving the addition of trichlorosilane to 1- and 4-t-butylcyclohexene catalyzed by dichlorobis(ethylene)-μ,μ'-dichlorodiplatinum(II)[7].



(1)

Treatment of *either* 1- or 4-t-butylcyclohexene with trichlorosilane and the aforementioned platinum complex resulted in the formation of the terminal adduct, (A), 1-trichlorosilyl-2-(1-methylcyclohexyl)propane and compound B, which we have identified as a ring adduct*. The structure of A was established by a comparison

---

* The NMR and infrared spectra of this compound indicate that the tert-butyl group is present. Elemental analyses also check for a ring adduct. The exact ring isomer which this species represents has not yet been determined.

of its infrared and NMR spectra with those of an authentic sample prepared by the addition of trichlorosilane to 1-methyl-1-isopropenylcyclohexane[8]*.

When reaction (2) was catalyzed by dichlorobis(ethylene)-μ,μ'-dichlorodiplatinum(II) *both* compounds A and B were obtained. However, when benzoyl peroxide was substituted for the platinum complex in reaction (2), only compound A was produced. Equally as striking, the unreacted olefins recovered from every run (*i.e.* both in reactions (1) and (2)) involving the platinum complex catalyst consisted of an approximately equilibrium mixture of the t-butylcyclohexenes[9] together with small amounts of t-butylcyclohexane. No 1-methyl-1-isopropenylcyclohexeane could be detected** in these recovered olefins. This was true even in the case of the olefins recovered from reaction (2).

Table 1 summarizes the experimental results which were obtained.

Since the methyl group migrations observed were reminiscent of carbonium ion rearrangements, it was imperative to rule out the possibility that small amounts of dissolved hydrogen chloride were effecting the olefin isomerization and methyl group shifts. Accordingly, in two separate experiments, samples of 1-t-butylcyclohexene and 4-t-butylcyclohexene were mixed with equimolar amounts of trichlorosilane and heated to 140° (sealed tube) for 92 and 27 h respectively. No adduct formation or olefin isomerization was observed. In another control experiment, 4-t-butylcyclohexene was held at 100° for 19.5 h in the presence of the platinum complex catalyst. No double bond migration occurred. Hence, it can be concluded that the double bond and methyl group migrations are *not* caused either by dissolved hydrogen chloride or the catalyst alone.

An examination of the data in Table 1 indicates that methyl group migration may be favored by higher reaction temperatures. Thus, at reflux temperatures***, 4-t-butylcyclohexene seemed to undergo ring addition primarily, while at 140° considerably more methyl migration occurred to form terminal adduct. Another point of interest is the relatively slow rate of reaction of the 1-t-butylcyclohexene relative to the 4-isomer, although both compounds produce terminal adduct *via* a methyl group migration.

Since rather long reaction times and relatively high temperatures are needed to obtain the skeletal rearrangements observed, judgment must be reserved as to the mechanism and nature of the active catalyst in these reactions. Further investigations

---

* The 1-methyl-1-isopropenylcyclohexane we obtained from the published[8] preparative procedure was found to contain 7% of 1-t-butylcyclohexene upon v.p.c. analysis.

** The limit of our analytical method for the detection of this compound is *ca.* 0.5%. In a study[10] of the equilibration of an analogous system, vinylcyclohexane–ethylcyclohexenes, it was noted that no vinylcyclohexane was detectable at 25° and only 0.1% was present at 250°. It is not unlikely that minute quantities of 1-methyl-1-isopropenylcyclohexane are present in our recovered olefins but escape detection.

The v.p.c. analysis conditions consisted of a 10′ × ¼″ column packed with β,β'-oxydipropionitrile at 83°.

*** The initial temperature of the refluxing liquid was about 55°, slowly increasing as addition proceeded to a terminal value of 170° for reaction (1) and 90° for reaction (2).

TABLE 1

THE ADDITION OF TRICHLOROSILANE TO VARIOUS OLEFINS

Compound	*Conditions*[a]	*Yield*[b] (%)	*Product composition*[c] (%)	
			A[e]	*B*[f]
1-t-Butylcyclohexene	sealed tube 140°, 92 h	14	44	33
4-t-Butylcyclohexene	sealed tube 140°, 27 h	69	30	56
	reflux 114.5 h	62	8	77
1-Methyl-1-isopropenylcyclohexane	reflux 19 h	49	66	28
	reflux 20 h[d]	35	100	—

---

[a] The additions (except for last entry) were run using equimolar amounts of olefin and trichlorosilane at reflux in a closed system (mercury trap) or in 12 mm × 200 mm sealed tubes. The amount of the platinum complex used as catalyst in each case was *ca.* 2 mg. [b] The yield of adduct is based on distilled material and is calculated from the starting olefin, regardless of the amount of recovered alkene. [c] Based on v.p.c. peak areas. A 1/4″ × 10′ QF-1 column operated between 150–175°C was used. The difference between 100 and the percentage sums represents other (presumably isomeric) species present. [d] In this run, 0.05 mole of olefin, 0.1 mole of trichlorosilane and 0.005 mole of benzoyl peroxide in 50 ml of heptane was used. [e] Calcd. for $C_{10}H_{19}Cl_3Si$ [1-trichlorosilyl-2-(1-methylcyclohexyl)propane]: C, 43.88; H, 7.00; Cl, 38.87. Found: C, 43.81; H, 6.88; Cl, 39.15. [f] Calcd. for $C_{10}H_{19}Cl_3Si$ [t-butylcyclohexyltrichlorosilane]: as above. Found: C, 43.62; H, 6.79; Cl, 38.73.

are currently in progress on other systems which might undergo similar skeletal rearrangements in the hope that light can be shed on the reaction mechanism.

Acknowledgment

The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

Department of Chemistry, Purdue University,
West Lafayette, Indiana (U.S.A.)

ROBERT A. BENKESER
ROBERT F. CUNICO

1 J. L. SPEIER, J. A. WEBSTER AND G. H. BARNES, *J. Am. Chem. Soc.*, 79 (1957) 974.
2 J. C. SAAM AND J. L. SPEIER, *J. Am. Chem. Soc.*, 80 (1958) 4104.
3 J. C. SAAM AND J. L. SPEIER, *J. Am. Chem. Soc.*, 83 (1961) 1351.
4 J. W. RYAN AND J. L. SPEIER, *J. Am. Chem. Soc.*, 86 (1964) 895.
5 M. C. MUSOLF AND J. L. SPEIER, *J. Org. Chem.*, 29 (1964) 2519.
6 T. G. SELIN AND R. WEST, *J. Am. Chem. Soc.*, 84 (1962) 1863.
7 A. J. CHALK AND J. F. HARROD, *J. Am. Chem. Soc.*, 87 (1965) 16.
8 H. PINES AND J. MARECHAL, *J. Am. Chem. Soc.*, 77 (1955) 2819.
9 R. A. BENKESER, R. K. AGNIHOTRI, M. L. BURROUS, E. M. KAISER, J. M. MALLAN AND P. W. RYAN, *J. Org. Chem.*, 29 (1964) 1313.
10 J. HERLING, J. SHABTAI AND E. GIL-AV, *J. Am. Chem. Soc.*, 87 (1965) 4107.

Received May 31st, 1966