to contain 0.138 g (33%) of 1-propanol, 0.187 g (46%) of allyl alcohol, and 0.185 g (23%) of allyl propionate.

**N,N′-Dipropionyl-N,N′-diallyloxyhydrazine with Sodium Hydrosulfite.** A solution of 0.50 g (0.00193 mol) of the hydrazine and 1.0 g (0.0048 mol) of sodium hydrosulfite in 15 ml of methanol and 10 ml of water was stirred for 25 min. The reaction mixture was found to contain 0.08 g (26%) of allyl alcohol and 0.28 g (63%) of allyl propionate by glpc.

**N,N′-Diacetyl-N,N′-di-*p*-nitrobenzyloxyhydrazine with Chlorine.** Chlorine was bubbled into 1.82 g (0.00435 mol) of the hydrazine in 75 ml of 1:1 carbon tetrachloride–chloroform mixture for 30 min. The solution was distilled, and the first 4 ml showed an infrared spectrum identical with acetyl chloride. From the distillate acetamide was prepared by addition of concentrated ammonia. From the residue 0.40 g (31%) of a solid, mp 211.5–213°, shown to be *p*-nitrobenzaldehyde di-*p*-nitrobenzyl acetal[12] and 1.02 g (61%) of *p*-nitrobenzyl acetate wei e separated.

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# The Addition of Trichlorosilane to Cyclic Olefins

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*Contribution from the Chemical Laboratories of Purdue University, West Lafayette, Indiana 47907.* *Received September 28, 1967*

**Abstract:** The addition of trichlorosilane, in the presence of chloroplatinic acid, to 1-, 3-, and 4-ethylcyclohexenes as well as to ethylidene- and vinylcyclohexanes was studied in detail. In every case, the major product was 2-cyclohexylethyltrichlorosilane. In the reaction with the ethylcyclohexenes, the recovered olefin fraction was found to contain all the possible monoolefin isomers except vinylcyclohexane. Contrary to reports, 1-*n*-propylcyclohexene also adds trichlorosilane in the presence of chloroplatinic acid to form 3-cyclohexylpropyltrichlorosilane. The unchanged olefins recovered from this reaction are composed again of a mixture of the various isomers. The above findings now eliminate the necessity for invoking anything but a smooth, consecutive double-bond shift along the chain in these cyclic systems as suggested by the mechanism of Harrod and Chalk. Platinum complexes, like dichlorobis(ethylene)-$\mu,\mu'$-dichloro-diplatinum(II) and dichlorobis(ethylcyclohexene)-$\mu,\mu'$-dichloro-diplatinum(II), were also effective catalysts in producing terminal adducts in the reaction of 1-ethylcyclohexene with trichlorosilane, while platinum on charcoal was not. This, in conjunction with other qualitative observations which were made, suggests that a soluble platinum complex, rather than platinum metal itself, is the active catalyst in such systems.

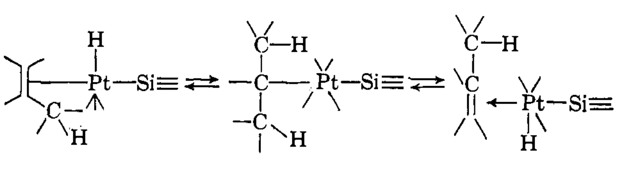
In 1957, Speier and coworkers[2] made the important discovery that certain silicon hydrides, like trichlorosilane, added to 2-pentene in the presence of catalysts like chloroplatinic acid to form the same terminal adduct as that obtained from 1-pentene.

$$\text{1- or 2-pentene} \xrightarrow[H_2PtCl_6]{SiHCl_3} CH_3(CH_2)_4SiCl_3$$

Since the advent of this discovery, numerous papers[3] have appeared relating to the scope of this transformation and the possible mechanism involved.

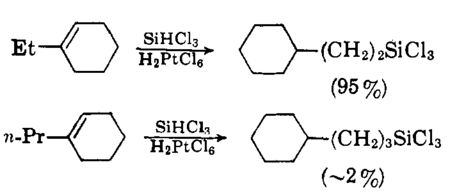
Recently a mechanism was proposed[4] for these reactions which in essence involved the reversible formation of a $\pi$ complex between the transition metal and the double bond of the olefin, followed by another reversible interconversion between the $\pi$ complex and a $\sigma$ complex. The latter would involve a direct bond between the metal atom and one of the carbon atoms composing the original olefin linkage. This mechanism would predict a stepwise migration of the double bond down an alkyl chain by progressive hydrogen shifts *via* the intermediacy of the platinum atom.

The similarity between this mechanism and that proposed for the "oxo" reaction has been pointed out.[5]



Recently it has also been shown that silane additions can be catalyzed by iron pentacarbonyl[6] and a dicobalt octacarbonyl[7] which supports the analogy drawn with the "oxo" process.

It came to our attention that there was at least one report[8] in the literature which suggested that the double-bond migration in such silane additions was not occurring by smooth, successive shifts down a chain. Thus, it was reported that 1-ethylcyclohexene reacts with trichlorosilane and chloroplatinic acid to form terminal adduct in 95% yield, but that 1-*n*-propylcyclohexene was essentially unreactive under the same conditions.



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(1) National Chemical Laboratory, Poona, India.

(2) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, 79, 974 (1957).

(3) For example, see M. R. Stober, M. C. Musolf, and J. L. Speier. *J. Org. Chem.*, 30, 1651 (1965), and previous papers in this excellent series.

(4) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

(5) J. F. Harrod and A. J. Chalk, *ibid.*, **87**, 1133 (1965).

(6) A. N. Nesmeyanov, R. Kh. Freidlina, E. C. Chukovskaya, R. G. Petrova, and A. B. Belyavsky, *Tetrahedron*, **17**, 61 (1962).

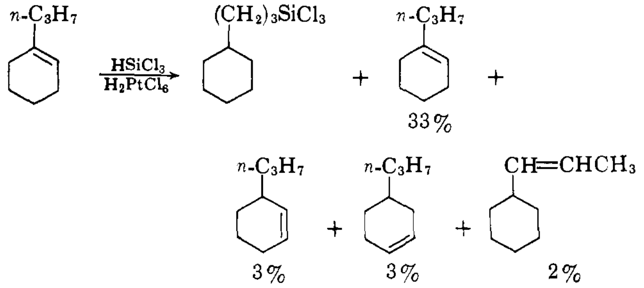
(7) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(8) T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

Likewise, 1-methylcyclohexene, under the same reaction conditions, gave terminal adduct and 4-methylcyclohexene, while the latter olefin gave terminal adduct and 1-methylcyclohexene. Significantly, no 3-methylcyclohexene was detected in either of these reaction products. In order to accommodate these experimental findings, it was postulated that 1,3-type hydrogen shifts were occurring in these systems.

A consideration of the Chalk and Harrod mechanism would lead to the conclusion that 1-*n*-propylcyclohexene should react in a fashion similar to 1-ethylcyclohexene–resulting in terminal adduct and isomerization of the olefin.

In a reexamination of the above work,[8] we found that, under suitable conditions, 1-*n*-propylcyclohexene does indeed add trichlorosilane in the presence of chloroplatinic acid. In addition to terminal adduct, all possible monoolefin isomers could be detected in the reaction product except propylidenecyclohexane and allylcyclohexane.[9]

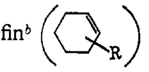


If a large excess of trichlorosilane were used in the reaction, very poor yields of adduct were obtained, possibly because the reflux temperature of the mixture was too low. When only a slight excess of trichlorosilane was used (silane:olefin ratio, 1.3:1), the temperature of the refluxing reaction mixture was higher and addition occurred. It is quite possible this is the reason the earlier workers[8] observed no addition under their conditions.

The results with 1-*n*-propylcyclohexene prompted us to investigate the addition of trichlorosilane to the ethylcyclohexenes (Table I). Using pure samples of 1-, 3-, and 4-ethylcyclohexenes, vinylcyclohexane, and ethylidenecyclohexane, it was found that in every case 2-cyclohexylethyltrichlorosilane was obtained. When an addition of trichlorosilane to 1-ethylcyclohexene was carried out for 3.5 hr, a 17% yield of terminal adduct was obtained and the recovered olefin fraction was shown to contain *all* the possible isomeric olefins except vinylcyclohexane (Table I). Essentially the same results were obtained with 3- and 4-ethylcyclohexenes.

If one assumes that olefin isomerization in such addition reactions tends toward a thermodynamic[10] distribution of isomers, the absence of vinylcyclohexane in our recovered olefin mixtures is not surprising. We have demonstrated that vinylcyclohexane reacts vigorously with trichlorosilane in the presence of chloroplatinic acid to form terminal adduct. Secondly, it has been shown[11] that, even at 250°, only 0.1% of vinylcyclohexane exists in equilibrium with the other olefins in this series.

Table I. Chloroplatinic Acid Catalyzed[a] Addition of Trichlorosilane to Ethylcyclohexene Series

| Olefin[b]  R = | Reaction time, hr | Yield of adduct,[c] % |
|---|---|---|
| 1-Ethyl | 23 | 74 |
| 1-Ethyl[d] | 3.5 | 17 |
| 3-Ethyl | 96 | 83 |
| 3-Ethyl[e] | 3.5 | 19 |
| 4-Ethyl | 12 | 88 |
| 4-Ethyl[f] | 6 | 59 |
| 4-Ethyl[g] | 3.5 | 18 |
| Ethylidenecyclohexane | 75 | 69 |
| Vinylcyclohexane | 0.5 | 68 |

[a] Amount of catalyst used in each run was 0.5 ml of a solution in 2-propanol which contained 0.025 g of $H_2PtCl_6 \cdot 6H_2O$. [b] Olefin–$SiHCl_3$ ratio in each run was 1:1.9. [c] In every case the adduct obtained was at least 95% terminal. [d] In this run, the recovered volatiles contained 18% ethylcyclohexane, 60% 1-ethylcyclohexene, 5% 3- and 4% 4-ethylcyclohexanes, 7% ethylidenecyclohexane, and 6% ethylbenzene. [e] The recovered volatiles contained 15% ethylcyclohexane, 66% 1-ethylcyclohexene, 4% total of 3- and 4-ethylcyclohexenes, 6% ethylidenecyclohexane, and 8% ethylbenzene. [f] The recovered volatiles contained 14% ethylcyclohexane, 16% 1-ethylcyclohexene, and 2% each of 3- and 4-ethylcyclohexenes. [g] Recovered volatiles contained 2% ethylcyclohexane, 71% 1-ethylcyclohexene, 13% 3- and 4-ethylcyclohexenes, and 11% ethylidenecyclohexane.

It must be noted that, while our experimental data are in agreement with the predictions of the Harrod and Chalk mechanism involving an unlimited series of consecutive double-bond shifts, they do not *preclude* other possibilities.[12] It is simply that our findings allow an alternate interpretation for existing data which previously had been explained in other ways.

The nature of the catalyst in these systems presents a complex and intriguing problem which still remains to be solved. Several experiments were carried out during the course of this investigation which tend to shed some light on this question.

When a mixture of ethylcyclohexane, trichlorosilane, and chloroplatinic acid in 2-propanol was heated with-

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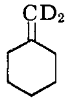
(9) The analytical problem here is quite severe in that these two compounds have retention times (vpc) quite close to the other components in the mixture. In view of our results in the ethylcyclohexene series (see above) wherein we were able to detect ethylidenecyclohexane in the reaction products, we strongly suspect that propylidenecyclohexane is present here also in at least minute quantities.

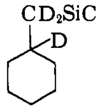
(10) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964).

(11) J. Herling, J. Shabtai, and E. Gil-Av, *J. Am. Chem. Soc.*, **87**, 4107 (1965).

(12) A referee has pointed out that the experiment of Selin and West[8] in which 1-methyl-$d_3$-cyclohexene, when treated with excess trichlorosilane and chloroplatinic acid, yielded terminal adduct with no deuterium loss eliminates the possibility of



as an intermediate. It should be noted, however, that the Chalk–Harrod mechanism would allow such a result should the formulation of the terminal adduct be



Since the positions of the deuterium atoms in the adduct were not determined,[8] this still remains a possibility. It must be admitted that the Chalk–Harrod mechanism would also likely predict that *some* deuterium exchange should occur in this case. Since *extensive* deuterium exchange was observed [J. W. Ryan and J. L. Speier, *J. Am. Chem. Soc.*, **86**, 896 (1964)] in the same system using trichlorosilane-*d*, we feel that definitive conclusions based on deuterium-exchange work are premature at this time.

out an olefin present, a precipitate formed on the walls of the flask within an hour. The precipitate, after decantation and washing,[13] was shown by appropriate qualitative tests to contain platinum metal. The *clear* filtrate (but *not* the precipitate) would catalyze the addition of trichlorosilane to 1-ethylcyclohexene. The precipitate, on the other hand, did catalyze the addition of trichlorosilane to allylcyclohexane. In this respect, platinum on charcoal also catalyzed the addition of trichlorosilane to allylcyclohexane, but was ineffective as a catalyst for a similar addition to 1-ethylcyclohexene. These results would seem to indicate that a soluble complex was the active catalyst.[14]

Further, we synthesized the platinum complex, dichlorobis(ethylcyclohexene)-$\mu,\mu'$-dichloro-diplatinum(II),[15] and found it to be dimeric in structure by analysis and molecular weight. This material likewise catalyzed the addition of trichlorosilane to 1-ethylcyclohexene and allylcyclohexane. In a similar fashion, dichlorobis(ethylene)-$\mu,\mu'$-dichloro-diplatinum(II)[16] was a very effective catalyst for the addition of trichlorosilane to *both* 1-ethylcyclohexene and allylcyclohexane.

The foregoing data taken as a composite, while not conclusive, are strongly suggestive of a soluble platinum complex being the active catalysts in these reactions.

## Experimental Section

**1-Ethylcyclohexene and 1-*n*-Propylcyclohexene.** These compounds were prepared by the reaction of the appropriate Grignard reagent with cyclohexanone followed by iodine-catalyzed dehydration of the resulting alcohols.[17] After distillation, the products had physical constants in agreement with the reported values.[18,19]

**3-Ethylcyclohexene and 3-*n*-Propylcyclohexene.** These compounds were prepared by coupling 3-bromocyclohexene[20] with the appropriate Grignard reagent.[21] The physical constants of these olefins were in agreement with the reported values.[22]

**Vinylcyclohexane** was prepared by reduction of 2-phenylethanol at 2000-psi hydrogen pressure with W-7 Raney[23] nickel as catalyst. The product, 2-cyclohexylethanol, possessed physical properties in accord with published values.[24] Acetylation of this alcohol in carbon tetrachloride gave 2-cyclohexylethyl acetate (bp 217–218°; $n^{20}\mathrm{D}$ 1.4494 (lit.[25] bp 97–98° (15 mm); $n^{20}\mathrm{D}$ 1.4478). Pyrolysis (490°) of the latter in a 1-in. Pyrex tube packed with 12 in. of glass helices gave vinylcyclohexane, bp 125°; $n^{20}\mathrm{D}$ 1.4481 (lit.[25] bp 125°; $n^{20}\mathrm{D}$ 1.4470).

**4-Ethylcyclohexene.** *p*-Ethylphenol was hydrogenated catalytically with W-7 Raney nickel[23] at 1900–2000 psi to give 4-ethylcyclohexanol, bp 192–194°; $n^{20}\mathrm{D}$ 1.4633 (lit.[26] bp 191–192°; $n^{20}\mathrm{D}$ 1.4640). Acetylation of the alcohol in carbon tetrachloride gave 4-ethylcyclohexyl acetate, bp 207–210°; $n^{20}\mathrm{D}$ 1.4431 (lit.[22] bp 209–211°; $n^{20}\mathrm{D}$ 1.4430). This ester was pyrolyzed as described above to give 4-ethylcyclohexene, bp 131–132°; $n^{20}\mathrm{D}$ 1.4490 (lit.[27] bp 133°; $n^{20}\mathrm{D}$ 1.4490).

**Ethylidenecyclohexane.** This olefin was prepared by the general method of Wittig.[28] Ethyltriphenylphosphonium bromide[29] was converted to its ylide with phenyllithium, followed by condensation with cyclohexanone to give ethylidenecyclohexane, bp 134.5–135°; $n^{20}\mathrm{D}$ 1.4619 (lit. bp 134.5°;[30] $n^{20}\mathrm{D}$ 1.4623[31]).

**Allylcyclohexane** was prepared by coupling allyl chloride with cyclohexylmagnesium chloride, bp 147–148°; $n^{20}\mathrm{D}$ 1.4531 (lit.[32] bp 149–151°; $n^{20}\mathrm{D}$ 1.454).

**Ethylcyclohexane.** High-pressure catalytic hydrogenation (1500 psi) of ethylbenzene using a Raney nickel catalyst (W-7[23]) gave ethylcyclohexane, bp 130°; $n^{20}\mathrm{D}$ 1.4324 (lit.[33] bp 129–130°; $n^{20}\mathrm{D}$ 1.4324).

**Vinylcyclohexane and Ethylidenecyclohexane.** Cyclohexylmethylcarbinol was prepared by the addition of cyclohexylmagnesium bromide to acetaldehyde. The boiling point of the product was 78–80° (8.5 mm) ($r^{25}\mathrm{D}$ 1.4618) (lit.[34] bp 83–85° (9 mm); $n^{25}\mathrm{D}$ 1.4630). Acetylation with acetyl chloride in carbon tetrachloride gave the acetate boiling at 196–205°; $n^{25}\mathrm{D}$ 1.4439 (lit.[35] bp 92–93 (18 mm); $n^{25}\mathrm{D}$ 1.4425). Pyrolysis (460–480°) of the acetate in a 1.5-in. Pyrex tube packed with 16 in. of glass beads gave a mixture of two olefins boiling at 125–135°. Analysis by vpc (di-*n*-butyl tetrachlorophthalate column at 130° or on silver nitrate–ethylene glycol at 32°) showed 75% vinylcyclohexane and 25% ethylidenecyclohexane.

**2-Cyclohexylethyltrichlorosilane.** An authentic sample of this material was prepared (68% yield) by the general hydrosilylation procedure described below using vinylcyclohexane and trichlorosilane. A vigorous reaction occurred during the addition of the silane, and the temperature rose spontaneously to 120°. The product boiled at 64° (0.2 mm) (lit.[8] bp 56–60° (0.1 mm)). Analysis by vpc (4-ft silicone gum rubber column) showed only one peak.

This material had an identical infrared spectrum with the major product obtained by treating 1-ethylcyclohexene with trichlorosilane and chloroplatinic acid. The structure of the latter product had been established[8] as 2-cyclohexylethyltrichlorosilane.

**3-Cyclohexylpropyltrichlorosilane.** An authentic sample of this material was prepared (44% yield) by the general hydrosilylation procedure described below using allylcyclohexane and trichlorosilane. The product boiled at 78–80° (0.6 mm).

*Anal.* Calcd for $C_9H_{17}Cl_3Si$: C, 41.62; H, 6.60; Cl, 40.96. Found: C, 41.94; H, 6.45; Cl, 40.58.

3-Cyclohexylpropyltrichlorosilane was also produced in 30% yield by refluxing, for 72 hr, a mixture of allylcyclohexane (80.5 mmol) with trichlorosilane (167 mmol) in 21 g of cyclohexane containing 1.5 g of benzoyl peroxide. The material obtained by this route was identical in all respects (boiling point, gas chromatography retention time, infrared spectrum) with that obtained above by the general hydrosilylation procedure.

**General Procedure for the Addition of Trichlorosilane to Olefins.** A 100-ml, three-necked flask fitted with a Friedrichs condenser and thermometer was flushed thoroughly with dry nitrogen. The appropriate olefin (0.1 mol) and 0.5 ml of a solution of chloroplatinic acid in 2-propanol (containing 0.025 g of $H_2PtCl_6 \cdot 6H_2O$) were charged into the flask. Trichlorosilane (25.0 g, 0.19 mol) was distilled into the flask. During this addition the reaction mixture

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(13) We recognize the possibility that our washing procedure may have effected the decomposition of the original material comprising the precipitate to platinum metal. However, the washing was deemed necessary at this point to remove the last traces of the filtrate which we have shown *does* catalyze this addition.

(14) Unfortunately, an alternate explanation remains—that trace amounts of unreacted chloroplatinic acid remain dissolved and, after filtration, again function as a catalyst in the usual fashion.

(15) While we prepared this material from 1-ethylcyclohexene, it is not inconceivable that it is the 3- or 4-olefin isomer which is actually coordinated. Since it was outside the scope of this research to investigate the structure of this complex, we have chosen to name it simply as a derivative of ethylcyclohexene.

(16) J. Chatt and M. L. Searle, "Inorganic Syntheses," Coll. Vol. V. T. Moeller, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1957, p 210.

(17) P. D. Bartlett and R. H. Rosenwald, *J. Am. Chem. Soc.*, **56**, 1990 (1934).

(18) O. Wallach, *et al.*, *Ann.*, **360**, 48 (1908).

(19) M. Mousseron, R. Richaud, and R. Granger, *Bull. Soc. Chim. France*, **13**, 222 (1946).

(20) K. Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

(21) P. Ryan, Ph.D. Thesis, Purdue University, 1959.

(22) A. Berlande, *Bull. Soc. Chim. France*, **9**, 644 (1942).

(23) H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 176.

(24) N. Zelinsky, *Ber.*, **41**, 2628 (1908).

(25) R. Y. Levina and N. N. Mezentsova, *Uch. Zap. Mosk. Gos. Univ., Org. Khim.*, 7, 241 (1950); *Chem. Abstr.*, **49**, 3847 (1955).

(26) H. E. Ungnade and A. D. McLaren, *J. Am. Chem. Soc.*, **66**, 118 (1944).

(27) S. W. Ferris, "Handbook of Hydrocarbons," Academic Press Inc., New York, N. Y., 1955, p 32.

(28) G. Wittig and U. Schoellkopf, *Org. Syn.*, 40, 66 (1960).

(29) G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

(30) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, 80, 1425 (1958).

(31) J. R. van der Bij and E. C. Kooyman, *Rec. Trav. Chim.*, 71, 837 (1952).

(32) R. Y. Levina and D. M. Trakhtenberg, *J. Gen. Chem. USSR*, **6**, 764 (1936); *Chem. Abstr.*, 30, 6338 (1936).

(33) S. V. Lebedev and N. A. Skawronskaya, *J. Russ. Phys. Chem. Soc.*, **43**, 1124 (1911); *Chem. Zentr.*, **831**, 1440 (1912).

(34) J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962).

(35) W. K. Johnson, *J. Org. Chem.*, **24**, 865 (1959).

became pale yellow to orange in color, and the temperature rose to 45–50°.

A glass stopper was inserted into the third neck, and the mixture was heated under reflux for the specified period of time. During the course of the reaction the color deepened, but the reaction mixture remained homogeneous in appearance. Nitrogen pressure was maintained by means of an inlet tube attached to the condenser and a bubbler. In order to prevent trichlorosilane leakage, it was necessary to clamp the glass stopper and thermometer adaptor. A very rough estimate of the progress of the reaction could be obtained by noting the temperature rise of the reaction mixture.

After the specified reflux time had elapsed, the flask was allowed to cool and its contents transferred to a 50-ml, round-bottomed flask for fractionation. After removal of the low-boiling material (mostly trichlorosilane), the residue was fractionally distilled *in vacuo*. The fractions were then analyzed by vapor phase chromatography.

Chromatograms were obtained with an F & M 500 programmed-temperature gas chromatograph. In the ethylcyclohexene series, the saturated hydrocarbons, olefins, and aromatics were analyzed first on a 30-ft polypropylene glycol column at 100°. This column was not totally satisfactory for complete separation of the olefins, so the analysis was then carried out on a 6-ft 30% $AgNO_3$–glycol column[12,36] at 32–35° (injection port at 155°). In the *n*-propylcyclohexene series, a 20-ft di-*n*-butyl tetrachlorophthalate column was used at 130° for the olefins, saturated compounds, and aromatics. Either an 8-ft QF-1 column or a 4-ft silicone rubber column was used at 150° for identification of the trichlorosilyl adducts.

**Platinum-Catalyzed Addition of Trichlorosilane to 1-*n*-Propylcyclohexene.** 1-*n*-Propylcyclohexene (12.4 g, 0.10 mol) and 25.0 g (0.19 mol) of trichlorosilane were refluxed with 0.025 g of chloroplatinic acid in 2-propanol as catalyst. After 162-hr reflux, the temperature rose to 103°. The volatiles were removed, and the residue was distilled to give two fractions. Analysis (vpc) of the olefin fraction, 6.0 g, bp 151–156°, showed it to contain *n*-propylcyclohexane (6%), 1-*n*-propylcyclohexene (33%), 1-cyclohexyl-1-propene (2%), 3-*n*-propylcyclohexene (3%), 4-*n*-propylcyclohexene (3%), and *n*-propylbenzene (2%). The second fraction gave 7.8 g (30%) of adducts, bp 69–72° (0.2 mm). Analysis (vpc) indicated that the product was 93% 3-cyclohexylpropyltrichlorosilane and 7% of unidentified isomeric adducts. The major component was isolated by preparative-scale vpc. Its retention time and infrared spectrum were identical with those of the authentic sample prepared from allylcyclohexane.

When a run was carried out using 10.0 g (0.08 mol) of freshly prepared olefin and 13.0 g (0.1 mol) of trichlorosilane for 70-hr reflux, there was obtained 12.0 g (58%) of 3-cyclohexylpropyltrichlorosilane, bp 112° (5 mm). This product was confirmed by a comparison of retention time and infrared to an authentic sample.

**Dichlorobis(ethylcyclohexene)-$\mu,\mu'$-dichloro-diplatinum(II).** Platinic chloride was prepared[37] by heating chloroplatinic acid in a chlorine atmosphere at 275°. One gram of the freshly prepared platinic chloride was partially dissolved with 12 ml of glacial acetic acid. 1-Ethylcyclohexene (1.5 ml) was added to the suspension, which dissolved to give a dark brown clear solution. After about 5 min, a precipitate formed. This was filtered, and the filtrate was treated with more 1-ethylcyclohexene, but further precipitation did not occur. The precipitate was suspended in 10.0 ml of glacial acetic acid and triturated with 0.5 ml of 1-ethylcyclohexene. Filtration gave a pale green solid, which was crystallized from chloroform–cyclohexane. The first two crops were greenish black in color and were contaminated with platinum metal. The third crop which separated after allowing the solution to stand for 2 days was yellow in color and uncontaminated with platinum metal. It was recrystallized from chloroform–cyclohexane to give yellowish orange crystals, mp 130° dec. The complex is soluble in chloroform but not in water. It is stable in air and is not hygroscopic.

*Anal.* Calcd for $C_{16}H_{28}Pt_2Cl_4$: C, 25.55; H, 3.72; Cl, 18.90; mol wt, 752. Found: C, 25.87; H, 3.72; Cl, 18.63; mol wt, 748.

**Reaction of Ethylcyclohexane, Trichlorosilane, and Chloroplatinic Acid.** A mixture of ethylcyclohexane (11.2 g, 0.1 mol), 0.5 ml of a solution of chloroplatinic acid in 2-propanol (0.025 g of $H_2PtCl_6 \cdot 6H_2O$), and 25.0 g (0.19 mol) of trichlorosilane was refluxed for 96 hr. Within 1 hr after start of reflux, an orange precipitate had formed on the sides of the flask, and the supernatant liquid became clear. The low-boiling materials were removed, and the residue was distilled to give 10.7 g (96%) of recovered cyclohexane, bp 128.5–129.5°. Analysis (vpc) showed no olefins were present.

The precipitate that remained in the reaction flask was washed with acetone and ether and the resulting gray powder dissolved in *aqua regia*. The *aqua regia* solution was evaporated to dryness, the residue dissolved in concentrated hydrochloric acid, and this solution evaporated to dryness. This residue was taken up in water to give a clear yellow solution. Addition of potassium chloride or ammonium chloride gave a yellow precipitate and addition of potassium iodide solution produced a red-brown color.[38] It was concluded that the precipitate was platinum metal.

**Reaction of 1-Ethylcyclohexene with Filtrate from Ethylcyclohexane, Trichlorosilane, and Chloroplatinic Acid.** Ethylcyclohexane (11.2 g, 0.1 mol), chloroplatinic acid (0.025 g in 2-propanol), and trichlorosilane (25.0 g, 0.19 mol) were refluxed for 19 hr to give an orange solution containing an orange precipitate. The supernatant liquid was transferred under nitrogen to a flask containing 11.0 g (0.10 mol) of 1-ethylcyclohexene. The resulting solution was clear and pale yellow in color. The mixture was refluxed for 167 hr, during which time the temperature rose to 72°. The volatiles were removed *via* distillation and the residue distilled to give two fractions. The olefin fraction, 15.8 g, bp 126–130°, contained 94% ethylcyclohexane, 41% 1-ethylcyclohexene, 5% 3-ethylcyclohexene, and 2% 4-ethylcyclohexene. The adduct fraction, 9.2 g, bp 74–76° (0.5–0.6 mm), contained 2-cyclohexylethyltrichlorosilane, identical in infrared spectrum and retention time with an authentic sample.

**Reaction of the "Platinum" Precipitate with Olefins and Trichlorosilane. 1-Ethylcyclohexene.** Ethylcyclohexane (11.2 g, 0.1 mol), trichlorosilane (25.0 g, 0.19 mol), and chloroplatinic acid (0.025 g in 2-propanol) were refluxed for 17 hr during which time the flask became coated with an orange precipitate.

The supernatant liquid was decanted and the precipitate washed successively with four 25-ml portions of ether, two 25-ml portions of acetone, and four 25-ml portions of ether. The entire operation was carried out under an atmosphere of nitrogen.

To the flask containing the precipitate (now gray in color) was added 11.0 g (0.1 mol) of 1-ethylcyclohexene and 25.0 g (0.19 mol) of trichlorosilane. The mixture was refluxed for 126 hr. After the usual work-up, there was a 100% recovery of pure 1-ethylcyclohexene.

**Allylcyclohexane.** The precipitate was formed in the manner described above and to this was added 6.2 g (0.05 mol) of allylcyclohexane and 13.5 g (0.10 mol) of trichlorosilane. Upon addition of the silane, the mixture began to reflux and continued for 30 min. It was then heated at reflux for an additional 5 hr. After removal of the lower boiling components, the residue was distilled to give 9.6 g (74%) of 3-cyclohexylpropyltrichlorosilane boiling at 78–80° (0.25 mm).

**Platinum–Charcoal-Catalyzed Hydrosilylation. 1-Ethylcyclohexene.** Using the general procedure described above, 1-ethylcyclohexene and trichlorosilane were refluxed for 164 hr with 0.5 g of 10% platinum charcoal as catalyst. A total of 97% of the 1-ethylcyclohexene could be recovered at the end of this time. The tarry pot residue yielded only a trace of 2-cyclohexylethyltrichlorosilane.

**Allylcyclohexane.** Hydrosilylation of 7.7 g (0.062 mol) of allylcyclohexane for 20 hr with 16.3 g (0.12 mol) of trichlorosilane and 0.25 g of 10% platinum–charcoal catalyst gave, after distillation, 9.7 g (60%) of 3-cyclohexylpropyltrichlorosilane boiling at 90–92° (0.6 mm).

**Hydrosilylation Using Dichlorobis(ethylene)-$\mu,\mu'$-dichloro-diplatinum(II). 1-Ethylcyclohexene.** In the usual manner, 7.5 g (0.067 mol) of 1-ethylcyclohexene was heated with 10.0 g (0.074 mol) of trichlorosilane in the presence of a trace (*ca.* 3 mg) of dichlorobis(ethylene)-$\mu,\mu'$-dichloro-diplatinum(II) as catalyst. The temperature reached 140° in 40 min and was held at this point for an additional 20 min. Distillation gave 1.5 g of recovered olefins and 13.0 g (80%) of terminal adduct, bp 68° (0.8 mm).

**Allylcyclohexane.** Using the usual procedure, 12.4 g (0.10 mol) of allylcyclohexane and 25.0 g (0.19 mol) of trichlorosilane were refluxed for 48 hr in the presence of 10 mg of dichlorobis(ethylene)-$\mu,\mu'$-dichloro-diplatinum(II). Distillation provided 21.0 g (81%) of

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(36) E. Gil-Av, J. Shabtai, and J. Herling, *J. Chromatog.*, **1**, 508 (1958); **8**, 349 (1962).

(37) M. S. Kharasch and T. A. Ashford, *J. Am. Chem. Soc.*, **58**, 1733 (1936).

(38) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XVI, Longmans, Green and Co., New York, N. Y., 1937, p 171.

3-cyclohexylpropyltrichlorosilane, bp 100° (3.0 mm). About 3.0 g of tarry pot residue remained in the distilling flask.

**Hydrosilylation Using Dichlorobis(ethylcyclohexene)-$\mu,\mu'$-dichloro-diplatinum(II). 1-Ethylcyclohexene.** A mixture of 7.5 g (0.068 mol) of 1-ethylcyclohexene, 9.5 g (0.07 mol) of trichlorosilane, and 10 mg of dichlorobis(ethylcyclohexene)-$\mu,\mu'$-dichlorodiplatinum(II) was refluxed for 70 min. After the usual work-up, there was obtained 12.6 g (75%) of 2-cyclohexylethyltrichlorosilane (structure confirmed by comparison of its infrared spectrum and retention time on gas chromatography with an authentic sample).

**Allylcyclohexane.** A mixture of 8.3 g (0.067 mol) of allylcyclohexane, 19 g (0.134 mol) of trichlorosilane, and 10 mg of the platinum complex was refluxed for about 48 hr. There was obtained 14 g (78%) of 3-cyclohexylpropyltrichlorosilane (structure confirmed by comparison of its infrared spectrum and retention time on gas chromatography with an authentic sample).

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# The Effect of Urea and Other Reagents on the Reactivity of Associated *p*-Nitrophenyl Laurate

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**Abstract:** The rate constants for basic hydrolysis of *p*-nitrophenyl laurate decrease with increasing initial concentration of ester in the range $10^{-6}$–$10^{-5}$ *M*. The ester molecules must hydrophobically bind to one another, thereby enclosing the ester groups within associated hydrocarbon chains where hydrolysis is retarded. The rate inhibition is appreciable; the second-order rate constant for basic hydrolysis of *p*-nitrophenyl laurate at $1.0 \times 10^{-5}$ *M* is almost three orders of magnitude smaller than that for *p*-nitrophenyl acetate. The hydrolysis of laurate ester in 0.1 *M* NaOH is accelerated by addition of *n*-butylurea, dioxane, urea, and tetramethylammonium bromide (with a decreasing order of effectiveness). The rate enhancements caused by the additives cannot be ascribed to a medium effect at the chemically reactive site because all four reagents inhibit hydrolysis of a short-chain ester, *p*-nitrophenyl acetate. Thus, while 8.0 *M* urea increases the rate of hydrolysis of *p*-nitrophenyl laurate ($1 \times 10^{-5}$ *M*) by a factor of 33, urea (3.7 *M*) decreases the rate of hydrolysis of *p*-nitrophenyl acetate 2.4-fold. The facilitated hydrolyses are consequently due to exposure of the ester groups to hydroxide attack as a result of perturbation or destruction of the substrate aggregates. The effect is similar to the unmasking of protein groups as a result of denaturation. The mechanism of the additive–aggregate interactions is discussed qualitatively.

The rate constants for basic hydrolysis of *p*-nitrophenyl laurate decrease with increasing initial concentration of ester in the range $10^{-6}$–$10^{-5}$ *M* (Figure 1). The simplest explanation for this finding is that the substrate molecules hydrophobically bind to one another, thereby enclosing the ester groups within associated hydrocarbon chains. Ester hydrolysis would be inhibited in such a situation.[1] The rate inhibition is appreciable; the second-order rate constant for basic hydrolysis of *p*-nitrophenyl acetate is 800 times larger than that for *p*-nitrophenyl laurate at $1.0 \times 10^{-5}$ *M*. We have used this phenomenon as a means of kinetically assaying the ability of reagents to interact with long hydrocarbon chains in water. If a reagent, such as urea, effectively destroys or perturbs the laurate ester aggregates, then a large rate increase could ensue upon addition of urea to the hydrolysis medium. The interaction of urea and related compounds with nonpolar groups in aqueous solutions has already been explored *via* thermodynamic measurements (solubility determinations),[2] but the sensitivity of this approach is poor. For example, urea (8 *M*) increases the solubility of toluene in water only 2.38-fold, whereas the kinetic effect of urea on laurate ester hydrolysis will be shown to be much larger than this. We have studied the effect of four additives (urea, *n*-butylurea, dioxane, and tetramethylammonium bromide) on the hydrolysis rate of associated *p*-nitrophenyl laurate.

## Experimental Section

**Materials.** Reagent grade urea, *n*-butylurea, and tetramethylammonium bromide were recrystallized from 95% ethanol, chloroform–benzene, and methanol, respectively. Each was carefully dried in a vacuum desiccator. Dioxane was distilled twice (once over $LiAlH_4$ and once from a solution of the sodium ketyl of benzophenone) immediately before use. The *p*-nitrophenyl laurate was used as obtained from the Pierce Chemical Co. The white crystals melted at 45–46.5° (lit.[3] mp 46°). The yield of *p*-nitrophenolate upon basic hydrolysis of the *p*-nitrophenyl laurate indicated a satisfactory purity of the ester. *p*-Nitrophenyl acetate had been prepared previously[4] and it melted at 77–78° (lit.[5] mp 77.5–78°).

**Kinetics.** The rate constants for hydrolysis of *p*-nitrophenyl laurate were obtained in the following manner. A 1.00-cm cuvette was filled with 3.00 ml of 0.1 *N* NaOH and equilibrated in a Cary 14 spectrophotometer set at 400.0 m$\mu$ (0.1–0.2 slide wire). After 10 min, 25 $\mu$l of an acetonitrile solution of *p*-nitrophenyl laurate was added by means of a small stirring rod flattened at on end. The increase in absorbance was then traced as a function of time. Pseudo-first-order plots are curved since the rate of the reaction accelerates as ester is destroyed (Figure 1). Therefore, absorbance–time data at the initial portion of the reactions had to be used to calculate the rate constants.[6] At the higher concentrations of ester, the $k_{\text{obsd}}$ *vs.* concentration curve (Figure 1) is relatively flat and

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[1] F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, **89**, 4698 (1967); M. T. A. Behme, J. G. Fullington, R. Noel, and E. H. Cordes, *ibid.*, **87**, 266 (1965).

[2] D. R. Robinson and W. P. Jencks, *ibid.*, **87**, 2462 (1965), and references cited therein.

[3] H. Zahn and F. Schade, *Chem. Ber.*, **96**, 1747 (1963).

[4] F. M. Menger, *J. Am. Chem. Soc.*, **88**, 3081 (1966).

[5] M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1652 (1957).

[6] K. J. Laidler, "The Chemical Kinetics of Enzyme Action," Oxford University Press, London, 1958, Chapter 3.