mole of 1,3-butadiene were added without mixing. The autoclave was closed, inverted to mix the reactants, rocked at room temperature for 24 hr., and then heated to 120° for 2 hr. After cooling, the vessel was opened, the product was extracted with hexane, and the hexane layer was washed with distilled water and dried over sodium sulfate. After removing the hexane, the product was separated on the preparative scale gas chromatograph.

The first component (18% yield) was identified as 5-nonanone. The gas chromatographic retention time and infrared spectrum were identical with an authentic sample prepared by the method of Briese and McElvain,[17] and the molecular weight (mass spectrum) was correct for 5-nonanone. The semicarbazone melted at 90°, lit.[16b] m.p. 90°, and showed no depression when mixed with the authentic derivative.

The second compound (9% yield) was identified as 3-nonen-5-one. The infrared spectrum contained adsorptions characteristic of ketone carbonyl and conjugated unsaturation, and the molecular weight (mass spectrum) was 140. Satisfactory elemental analysis was not obtained because of sensitivity to air as reported by Powell and Nielsen.[18] However, hydrogenation of the carbon–carbon unsaturation as described by Powell and Nielsen[18] yielded 5-nonanone. The infrared spectrum was identical with the authentic sample prepared above, the molecular weight (mass spectrum) was 142 (calcd. for 5-nonanone, 142), semicarbazone had m.p. 90° (lit.[16b] m.p. 90°), and mixture melting point of semicarbazone with authentic derivative was 90°.

The above experiment was repeated, and carbon monoxide gas was added to a pressure of 1200 p.s.i. before heating. The product, treated as before, yielded only one major component, 5-nonanone (25% yield), in the gas chromatograph.

In both of the above experiments, minor peaks were observed by gas chromatography but were not separated. These corresponded in retention time to *n*-valeraldehyde, 2-methyl-1-butanal, and vinylcyclohexene.

1-Butene Reaction.—Gaseous hydrogen tetracarbonylcobaltate(−I) was prepared by slowly dropping an aqueous solution of potassium tetracarbonylcobaltate(−I) into concentrated phosphoric acid under nitrogen. The acid solution was constantly stirred while nitrogen was bubbled slowly through the mixture.

The hydrogen tetracarbonylcobaltate(−I) formed was passed through a drying tube filled with calcium chloride, then precooled in a U-tube immersed in an ice bath. The gas mixture then was bubbled slowly through a mixture of 60 ml. of 1-butene (*ca.* 0.7 mole) and 10 ml. of pentane kept at −6 to −8°. The trap was fitted with a condenser kept at −30° to minimize loss of olefin. A 250-ml. solution of potassium tetracarbonylcobaltate(−I) containing approximately 0.12 mole of cobalt was used; thus, a large excess of olefin was present. This favors the formation of alkyl and acyl cobaltates(−I) and prevents the interaction of excess hydrogen tetracarbonylcobaltate(−I) with the above complexes to yield aldehydes.

After the gas had been bubbled through for 2–3 hr., the reddish solution was transferred rapidly to the autoclave under nitrogen, and the autoclave then was closed and heated between 120 and 130° for 3 hr. in order to decompose the carbonylcobaltates present.

The solution then was distilled, and the solvent and excess olefin were removed by aspirator vacuum. The high boiling product, 0.50 g., distilled below 40° (1 mm.).

The distillate was analyzed on a Perkin-Elmer 154-L gas chromatograph with a polyethyleneglycol distearate column. Peaks corresponding to *n*-valeraldehyde, 2-methylbutanal, 3,5-dimethyl-4-heptanone, 3-methyl-4-octanone, and 5-nonanone were observed.

An infrared spectrum of the distillate showed strong carbonyl absorptions around 5.8 μ.

Based on semiquantitative gas chromatographic estimates, the above compounds contribute roughly 80% of the product, the ketone to aldehyde ratio being about 9:1.

In another experiment, when no excess of olefin was present, this ratio was considerably smaller.

Acknowledgment.—We gratefully acknowledge the financial support received from the Esso Research and Engineering Company. We wish to thank Dr. J. B. Zachry and Dr. D. R. McAdams of Esso Research Laboratories, Baton Rouge, Louisiana, for help with some of the identifications.

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(17) R. R. Briese and S. M. McElvain, *J. Am. Chem. Soc.*, **55**, 1697 (1933).

(18) S. G. Powell and A. T. Nielsen, *ibid.*, **70**, 3627 (1948).

The Addition of Silicon Hydrides to Olefinic Double Bonds. IX. Addition of *sym*-Tetramethyldisiloxane to Hexene-1, -2, and -3

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sym-Tetramethyldisiloxane adds to either hexene-2 or hexene-3 in the presence of chloroplatinic acid to establish Si–C bonds with the silicon attached chiefly to the 1-position but also to the 2- and 3-positions of the hexyl group in the products. Hexene-1 formed the 1-hexyl derivative almost exclusively. During the reaction a hexene becomes a mixture of hexene isomers.

In the presence of platinum catalysts, chlorosilicon hydrides seem to add to acyclic olefins so as to form only primary alkylsilanes, even from olefins such as pentene-2,[1] heptene-3,[2] or 2-methylbutene-2.[3]

sym-Tetramethyldisiloxane behaves somewhat differently from the chlorosilanes in being able to form secondary alkylsilicon derivatives from an internal olefin. Heptene-3 apparently formed 1-, 3-, and 4-heptylsilicon compounds[2] by addition of *sym*-tetramethyldisiloxane.

During all such addition reactions isomerization of olefins may be observed.[3] Recent experiments with trichlorosilane-*d* (Cl_3SiD)[4] show that extensive exchange between Si–D and the C–H of the olefins accompany the isomerization. A plausible mechanism has been postulated[4] to rationalize these data. This mechanism seemed to indicate that a reaction that produced a 1-, a 3-, and a 4-heptylsilicon derivative from heptene-3 and tetramethyldisiloxane[2] must have produced also the 2-heptyl isomer. Heptene-3 also should have formed a mixture of the isomeric heptenes during the reaction. It was not observed to do so.[2]

To reconcile the earlier data[2] with more recent results,[4] essentially the same experiments were repeated using hexene-3, which was assumed to be chemically

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

(2) J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

(3) J. C. Saam and J. L. Speier, *ibid.*, **83**, 1351 (1961).

(4) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).

equivalent to heptene-3 for this purpose. To extend our data, hexene-1 and hexene-2 also were used.

In each experiment *sym*-tetramethyldisiloxane was added to one of the hexenes in the presence of chloroplatinic acid and converted into hexyltrimethylsilane as shown.

$$\text{Hexene} + O[SiMe_2H]_2 \xrightarrow{Pt} O[SiMe_2C_6H_{13}]_2$$

$$O[SiMe_2C_6H_{13}]_2 \xrightarrow[H_2SO_4]{NH_4Cl} 2ClSiMe_2C_6H_{13}$$

$$ClSiMe_2C_6H_{13} + MeMgBr \longrightarrow Me_3SiC_6H_{13}$$

Authentic samples of the 1-, 2-, and 3-hexyltrimethylsilanes were prepared. The ability of various vapor phase chromatography equipment was tested then for known mixtures of the three standards. No packed column available to us was able to separate the 2-hexyl from 3-hexyltrimethylsilane, although both of these were easily separable from the 1-hexyl isomer. Satisfactory separations of the three isomers were achieved with a capillary column. The column was then calibrated by means of the standards and used to gather the data in Table I.

TABLE I

1-, 2-, AND 3-TRIMETHYLSILYLHEXANES FROM THE ADDITION *sym*-TETRAMETHYLDISILOXANE TO HEXENE-1, -2, AND -3

	—% 1-, 2-, and 3-trimethylsilylhexane—		
Olefin	1-	2-	3-
Hexene-3[a]	76	10	14
Hexene-2[b]	88	7	5
Hexene-2[c]	87	7	6
Hexene-1[d]	99	Trace	None

[a] Addition was in a sealed tube at 100° 13 days. [b] Addition was in a sealed tube at 100° 19 days. [c] Addition was in a flask at reflux several days. [d] Addition was in a flask at reflux several hours.

These new data indicate that all the possible adducts form from hexene-2 or -3 with *sym*-tetramethyldisiloxane. Their separation was unambiguous and in each case excess hexene was recovered as a mixture of isomers. These new data indicate that the apparent absence of 2-heptylsilicon derivatives from the reaction of heptene-3 and tetramethyldisiloxane must be ascribed to inadequate analyses.

Experimental

Reagents.—Hexene-1 and hexene-2 were obtained from the Phillips Petroleum Company. Analysis by v.p.c. indicated that hexene-1 was at least 99% pure. Hexene-2 was a mixture of the *cis* and *trans* isomers containing a small amount of hexene-1. Hexene-3 was purchased from the Farchan Research Laboratory. V.p.c. and infrared analysis indicated it to be the *trans* isomer free of hexene-2 or -1. The catalyst was used as a 0.55 *M* solution of chloroplatinic acid hexahydrate in isopropyl alcohol.

Authentic samples of 1-, 2-, and 3-hexyltrimethylsilane were prepared. The first was made from 1-bromohexane, trimethylchlorosilane, and lithium in tetrahydrofuran below room temperature; the boiling point was 161.2°, n^{25}_{D} 1.4142, d^{25}_{4} 0.7474,[5] R_D 0.3345, calcd. 0.3382.

2-Hexyltrimethylsilane was prepared in the same manner from 2-bromohexane, b.p. 158.2°, n^{25}_{D} 1.4187, d^{25}_{4} 0.7494, R_D 0.3368, calcd. 0.3382.

3-Hexyltrichlorosilane was prepared by the addition of trichlorosilane to hexene-3 with benzoyl peroxide as the initiator essentially as previously described.[6] The 3-hexyltrichlorosilane was treated with excess methylmagnesium bromide in ether to give 3-hexyltrimethylsilane, b.p. 157.2° at 731 mm., n^{25}_{D} 1.4252, d^{25}_{4} 0.7597, R_D 0.3366, calcd. 0.3382.

Anal. Calcd. for 3-hexyltrimethylsitane: Si, 17.7. Found: Si, 17.2, 17.5.

Each of these samples was essentially pure by v.p.c. analysis and free from any isomers.

Analyses of mixtures of the 1-, 2-, and 3-hexyltrimethylsilanes were satisfactorily performed by a Perkin-Elmer Model 154C vapor phase chromatograph using nitrogen at 20 p.s.i. as the carrier and a 283 ft. × 0.02 in. stainless steel column with liquid paraffin N.F. as the adsorbent. A flame ionization detector was used with a Texas Instrument Company Recti/Riter recorder. A 2-μl. sample was split so that 1/500th passed through the column. Less than 1% of any of the isomers could be detected in mixtures of the three: retention times in minutes, 3-hexyl, 44.6 ± 0.4; 2-hexyl, 46.2 ± 0.5; 1-hexyl, 56.1 ± 0.4 at a column temperature of 40.5–41°.

Addition of *sym*-Tetramethyldisiloxane to Hexene-3.—Hexene-3 (11 g., 0.13 mole), *sym*-tetramethyldisiloxane (8.3 g., 0.62 mole), and 4.7 × 10^{-5} mole of chloroplatinic acid were heated in a 50-ml. ampule at 100° for 13 days. The mixture was devolatilized by removal of 2.7 g. of hexene. V.p.c. analysis of the recovered hexene showed it to be a mixture of isomers, mostly hexene-2 and -3.

The adduct (15.3 g.) was dispersed in 40 ml. of concentrated sulfuric acid, and ammonium chloride (10 g.) was stirred into the mixture in small portions. Hydrogen chloride was then bubbled through the mixture for 2 hr.

The top layer then was separated (18.5 g.) and added to methylmagnesium bromide (0.2 mole) in 140 ml. of ether. The mixture was heated to reflux 4 hr. and permitted to stand overnight. The mixture then was washed with dilute hydrochloric acid and then with water. The organic material was dried over calcium chloride and distilled to give a mixture of hexyltrimethylsilane (10.3 g., 65.7% over-all yield), n^{25}_{D} 1.4178–1.4140. The properties of the combined fractions are n^{25}_{D} 1.4150, d^{25}_{4} 0.7417, R_D 0.3376, calcd. 0.3382.

Anal. Calcd. for $C_9H_{22}Si$: Si, 17.7. Found: Si, 17.6, 17.7.

The distribution of isomers present in the mixture was determined by v.p.c. and was as indicated in Table I.

Addition of *sym*-Tetramethyldisiloxane to Hexene-2.—With the exception that hexene-2 was used, the preceding experiment was repeated. The reagents were heated at 100° for 19 days. A mixture of hexene (2.4 g.) was recovered, and distillation gave the hexyltrimethylsilanes (52% over-all yield), n^{25}_{D} 1.4160–1.4135. The properties of the combined fractions were n^{25}_{D} 1.4140, d^{25}_{4} 0.7399, R_D 0.3377, calcd. 0.3382.

Anal. Calcd. for $C_9H_{22}Si$: Si, 17.7. Found: Si, 17.9, 18.0.

The isomers in this mixture were as shown in Table I.

In order to see if essentially the same results would be obtained under different conditions, hexene-2 (134 g., 1.6 moles), *sym*-tetramethyldisiloxane (100.5 g., 0.75 mole), and 7.5 × 10^{-5} mole of chloroplatinic acid were heated to reflux for 144 hr.

Distillation of this mixture gave 38.3 g. of isomeric hexenes, essentially the same as previously obtained, and hexyltetramethyldisiloxane (22.9 g., 0.1 mole), n^{25}_{D} 1.4130, d^{25}_{4} 0.8088, R_D 0.3083, calcd., 0.3107.

Anal. Calcd. for $C_6H_{13}Me_2SiOSiMe_2H$: H (as SiH), 0.459. Found: H (as SiH), 0.455, 0.459.

V.p.c. analysis in a 0.25-in. packed column showed the presence of three compounds in this fraction, presumably the hexyl-1, -2, and 3-tetramethyldisiloxanes. They had nearly the same retention times, but did form three distinct closely spaced peaks on the chromatograph.

1,3-Dihexyltetramethyldisiloxane was obtained (126 g., 0.416 mole), n^{25}_{D} 1.4281, d^{25} 0.8126, R_D 0.3143, calcd. 0.3157.

Anal. Calcd. for $C_{16}H_{38}OSi_2$: Si, 18.54. Found: Si, 18.5, 18.5.

All of the fractions boiling above hexene were recombined (165 g.), including intermediate fractions and nonvolatile residues, and converted to hexyltrimethylsilanes as described before: n^{25}_{D} 1.4142, d^{25}_{4} 0.7422, R_D 0.3367, calcd. 0.3382. The isomers are shown in Table I.

Anal. Calcd. for $C_9H_{22}Si$: Si, 17.72. Found: Si, 17.7, 17.8.

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(5) F. C. Whitmore, L. H. Sommer, P. A. Di Giorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr [*J. Am. Chem. Soc.* **68**, 475 (1946)] report b.p. 163° at 760 mm., d^{20}_{4} 0.7422, n^{20}_{D} 1.4154.

(6) (a) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *ibid.*, **69**, 188 (1947); (b) J. L. Speier and J. A. Webster, *J. Org. Chem.*, **21**, 1044 (1956).

Addition of *sym*-Tetramethyldisiloxane to Hexene-1.—*sym*-Tetramethyldisiloxane (100.5 g., 0.75 mole) was added slowly (1.25 hr.) to refluxing hexene-1 (134 g., 1.6 moles) containing 7.5 × 10^{-5} moles of chloroplatinic acid. The reaction was noticeably exothermic. The mixture was kept at 140° for 4.5 hr. and distilled. The typical mixture of hexenes (17.1 g.) was recovered followed by 1,3-dihexyltetramethyldisiloxane (202 g., 90%), $n^{25}D$ 1.4265, d^{25}_4 0.8154, R_D 0.3142, calcd. 0.3157.

Anal. Calcd. for $C_{16}H_{38}OSi_2$: Si, 18.5. Found: Si, 18.6, 18.6.

This product was also converted to hexyltrimethylsilane as described; the properties are $n^{25}D$ 1.4132, d^{25}_4 0.7378, R_D 0.3379, calcd. 0.3382.

Anal. Calcd. for $C_9H_{22}Si$: Si, 17.7. Found: Si, 17.5, 17.9.

Acknowledgment.—The authors wish to express their appreciation to Robert Winger for assistance with analyses and to Joseph Cekada for making 1- and 2-hexyltrimethylsilanes.

Reactions of Enamines. IV. The Formation of Chloroiminium Salts from Certain Enamino Ketones[1]

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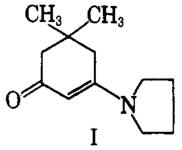
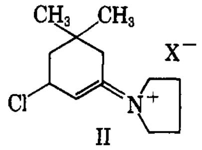
The reaction of enamino ketones with the acid chlorides of acids, the anions of which are also good leaving groups, or with phosphorus pentachloride, lead to chloroiminium salts. The proof of structure and mechanism of formation are discussed. A new synthesis of enamino ketones from β-chloro-α,β-unsaturated ketones is reported.

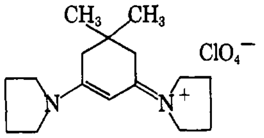
In our preliminary communication[2] it was shown that reaction of 5,5-dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one (I) with trichloroacetyl chloride gave N-(3-chloro-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium chloride (II, X = Cl) as a hygroscopic solid readily converted to the stable crystalline perchlorate II (X = ClO_4). The structure of II was established by its ultraviolet spectrum[3] (see Table I) and by facile reaction of its perchlorate with 1 mole of pyrrolidine to give the known N-(5,5-dimethyl-3-N′-pyrrolidylcyclohex-2-en-1-ylidene)pyrrolidinium perchlorate (III).[4] Further proof of the structure of II was provided by hydrolysis. The chloroiminium salt II was found to be extremely stable to hydrolysis with aqueous mineral acids (the preferred method for the hydrolysis of iminium salts[5]). Mild alkaline hydrolysis, however, afforded the known 3-chloro-5,5-dimethylcyclohex-2-en-1-one (IV).[6]



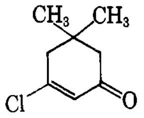
I



II

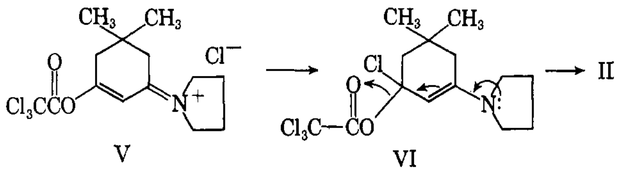


III



IV

It seemed to us, *ab initio*, that the formation of II must proceed by O-acylation of the enamino ketone I to the intermediate V.[7] Addition of chloride ion could then give VI from which the better leaving group (*i.e.*, trichloroacetate ion) would be eliminated.



It follows that the acid chloride of any acid, the anion of which is a good leaving group and a poor nucleophile, should undergo a similar reaction with I. To test this hypothesis, the enamino ketone I was heated with tosyl chloride in benzene solution. The hygroscopic salt, which was not fully characterized, gave II (X = ClO_4) in good yield when its aqueous solution was treated with perchloric acid or sodium perchlorate. In further support of our mechanism, picryl chloride underwent a similar reaction. Thus, reaction of I with picryl chloride in benzene solution, followed by treatment of the reaction mixture with water, afforded the picrate of the enamino ketone I and, as the minor product, the perchlorate II (X = ClO_4).

Indirect evidence for the reaction sequence is provided by reaction of I with diethylcarbamoyl chloride. It had been reported previously[8] that the enamino ketone I did not react with dimethylcarbamoyl chloride. While this may be true at lower temperatures, we have found that diethylcarbamoyl chloride reacts with I in refluxing chlorobenzene to give the N-(3-diethylamino-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium salt (VII), isolated as the perchlorate VII (X = ClO_4) and characterized by comparison of its physical properties with those of authentic material.[4]

The formation of VII can be rationalized by assuming reaction of the enamino ketone I with diethylcarbamoyl chloride to give the O-acylated intermediate VIII which can add chloride ion. Compound IX can then collapse to the chloroiminium cation, carbon dioxide,

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[1] Part III: A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 3492 (1963).

[2] G. H. Alt and A. J. Speziale, *Tetrahedron Letters*, 111 (1663).

[3] J. L. Johnson, M. E. Herr, J. C. Babcock, R. P. Holysz, A. E. Fonken, J. E. Stafford, and F. W. Heyl [*J. Am. Chem. Soc.*, **78**, 430 (1956)] have reported λ_{max} 274–278 mμ (ε >20,000) for ternary iminium salts of the type $>C{=}C{-}\overset{|}{C}{=}\overset{+}{N}<$; see also G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962).

[4] N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

[5] *Cf. inter alia:* G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

[6] A. W. Crossley and H. R. LeSueur, *J. Chem. Soc.*, **83**, 110 (1903).

[7] S. Hünig, E. Benzing, and E. Lücke [*Ber.*, **90**, 2833 (1957)] have observed the O-acylation of enamino ketones.