product. Fractional distillation of the organic layer gave 61 g., b.p. 63–98.5°, which was washed with concentrated sulfuric acid and then water, dried and fractionally distilled giving 48 g., 0.41 mole, 48% yield of *n*-propyltrimethylsilane,[28,29] b.p. 89–92°, n^{20} 1.3930.

---

[28] F. C. Whitmore, L. H. Sommer, P. D. George, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza and G. T. Kerr, This Journal, **68**, 475 (1946).

[29] H. Westermark, *Svensk Kem. Tidskr.*, **64**, 283 (1952), reported that the major products from the reaction of MeSi(OEt)$_3$ and Me$_2$Si(OEt)$_2$ with excess *n*-PrMgCl under forcing conditions were MePr$_2$SiOEt and Me$_2$PrSiOEt, respectively; however, small amounts of MeSiPr$_3$ and Me$_2$SiPr$_2$ also were obtained.

College of Chemistry and Physics
Pennsylvania State University
University Park, Pennsylvania

The Beckmann Rearrangement. VII. The Isolation and Rearrangement of 2,4,6-Trimethylacetophenone Oxime

By Frances Greer and D. E. Pearson

Received September 19, 1955

Previous failures to isolate the oximes of di-*o*-methyl substituted acetophenones have been summarized by Kadesch.[1,2] These are attributed to the difficulty of supplying correctly the additional energy necessary for the conversion of the aceto grouping to the *α*-oximinoethyl grouping (—C=NOHCH$_3$) in hindered structures.[1,3] In this conversion the *α*-oximinoethyl grouping is tilted out of the plane of the ring to a greater degree than the aceto grouping with proportionate loss of resonance interaction between the ring and side-chain.

Nevertheless, several facts suggest that these oximes might be isolated. The 2,4-dinitrophenylhydrazones of di-*o*-methyl substituted acetophenones have been reported recently.[4] And, a number of authors have reported that the Beckmann rearrangement products, the di-*o*-methyl substituted acetanilides, were isolated in attempts to make the corresponding oximes.[1,5,6] In other words, the oximes were formed, but conditions were strenuous enough to bring about rearrangement simultaneously.

We have attempted to isolate the oxime of 2,4,6-trimethylacetophenone (I) following ordinary procedures for oximation but extending the time of reactions considerably. The following comments summarize our experiences in twenty-five different attempts to prepare the oxime. Oximation was usually unsuccessful in aqueous solvents using either hydroxylamine hydrochloride and buffers or hydroxylamine-O-sulfonic acid,[7] although in two instances a 4% yield of oxime was obtained when using equal volumes of water and ethanol as a solvent for hydroxylamine hydrochloride. Oximation in ethanol buffered with sodium acetate gave 1–7% yields of the oxime. The best procedure was found to be oximation in anhydrous pyridine for one month at room temperature.[8] The yield of the oxime of I, a crystalline substance, was 40%.

Although precise rate data are not yet available, we are prepared to say at this time that the rate of rearrangement of the oxime of I is the fastest ever observed for any oxime. The rearrangement is at least 94% complete in 75 minutes at 0° in concentrated sulfuric acid. This rate can be compared with the half-lives of other oximes[3,9]

Oxime	Half-life, min.
Acetophenone	615 at 50.9°
o-Methylacetophenone	61 at 25°
Diisopropyl ketone	294 at 21.8°

The extremely rapid rate of rearrangement of the oxime of I supports the previous view[3] that the loss of coplanarity between the *α*-oximinoethyl grouping and the ring, detectable in *o*-methylacetophenone oxime, is approaching a maximum in the structure of the oxime of I. At this limit the side-chain will be tilted at right angles to the ring and maximum loss of resonance interaction between side-chain and ring will be incurred. Both results will facilitate the simultaneous bond-breaking and -making steps of the rearrangement.

Experimental

Preparation of 2,4,6-Trimethylacetophenone Oxime.—2,4,6-Trimethylacetophenone (I) (13.6 g., 0.084 mole) in 79 g. of carefully dried pyridine was added to a cooled solution of 34.8 g. (0.5 mole) of hydroxylamine hydrochloride in 79 g. of dry pyridine. The solution was allowed to stand for one month at room temperature in a well-stoppered container. The solution was then concentrated, b.p. 38–39° at 30 mm., until 140 ml. of pyridine was collected and to the point where severe bumping began. The residue was diluted with water to dissolve the pyridine hydrochloride. The heterogeneous solution, consisting of an oily phase above an aqueous phase, was refrigerated. Colorless crystals appeared in 24 hours at the interface of the two phases and apparently reached maximum growth in two weeks. The crystals were then removed by filtration, washed with water, and air-dried: 1.85 g. of the oxime of I, m.p. 98–100°. The filtrate and washings were combined and extracted with 100 ml. of benzene in 20-ml. portions. The benzene was extracted further with 235 g. of 10% aqueous sodium hydroxide in 5 portions. Neutralization of the alkaline extracts with Dry Ice gave 0.44 g. of oxime, m.p. 96–100°, after one recrystallization from aqueous alcohol. The extraction with sodium hydroxide was incomplete, however, as noted from the work-up of the benzene extracts. The benzene was removed at 30 mm. pressure and the oily residue, 10.9 g., seeded with a crystal of the oxime and allowed to stand. The crystals were removed by filtration after 24 hours, washed with small portions of ice-cold ethanol, and air-dried: 3.81 g. of the oxime of I, m.p. 97–100°. The total yield was 6.1 g., 40.3%. Crystallization to constant m.p. from aqueous ethanol gave colorless needles, m.p. 102.5–104°. Sublimation at reduced pressure neither raised nor sharpened the melting range. The oxime was unchanged after storage for several months although the m.p. range was lowered slightly.

Anal. Calcd. for $C_{11}H_{15}ON$: N, 7.90. Found: N, 7.75.

The Beckmann Rearrangement of 2,4,6-Trimethylacetophenone Oxime.—Finely powdered oxime (1.0 g.) was added to a stirred solution of 20 ml. of concentrated sulfuric acid maintained at 0°. Five minutes was required for the addition and solution of the oxime, during which time the temperature varied between 0 and 1°. (If the addition

---

[1] R. G. Kadesch, This Journal, **66**, 1207 (1944).

[2] The oxime of 2,3,4,6-tetramethylacetophenone has been reported, but the experimental details were not given in this paper: A. Claus and C. Foecking, *Ber.*, **20**, 3097 (1887).

[3] D. E. Pearson and E. D. Watts, *J. Org. Chem.*, **20**, 494 (1955). Paper VI and previous paper.

[4] D. E. Pearson and Frances Greer, This Journal, **77**, 1294 (1955); J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 2941 (1954).

[5] E. Feith and S. H. Davies, *Ber.*, **24**, 3546 (1891).

[6] A. E. Tchitchibabine, *Bull. soc. chim. France*, **51**, 1436 (1932).

[7] D. E. Pearson and Frances Ball, *J. Org. Chem.*, **14**, 118 (1949).

[8] Similar to the procedure of R. Jacquemain and P. Galliot, *Ann. chim.*, [12] **1**, 262 (1946).

[9] P. T. Scott, D. E. Pearson and L. J. Bircher, *J. Org. Chem.*, **19**, 1815 (1954).

was not made carefully, a violent and uncontrollable rearrangement reaction occurred.) The solution was then maintained at 0° for 70 minutes without stirring. The mixture was poured onto a slurry of ice and ammonium hydroxide. The white precipitate was removed by filtration, washed with water, and recrystallized from aqueous ethanol. After air-drying, 2,4,6-trimethylacetanilide was obtained as white needles: 0.85 g., m.p. 218–219°, mixed m.p. with authentic sample undepressed. An additional quantity of anilide was obtained from the mother liquors of the original recrystallization: 0.09 g., m.p. 217–218°. The total yield of 2,4,6-trimethylacetanilide was 0.94 g., 94%.

A second similar rearrangement, of 30-minute rather than 75-minute duration, using 0.50 g. of the oxime yielded 0.42 g. of the anilide contaminated with detectable amounts of unchanged oxime since the behavior on heating showed that softening commenced at 150° and melting occurred over the range 180–200°.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this work.

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE 5, TENN.

Reactions of Allylsilanes with Iodine

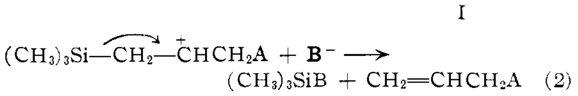
BY DANIEL GRAFSTEIN

RECEIVED AUGUST 17, 1955

In 1948, Pray, Sommer, *et al.*,[1] reported the facile cleavage of trimethylphenylsilane with bromine at 100° and the difficult cleavage of trimethylphenylsilane with iodine at reflux. Eaborn[2] refers to this paper as the first reported preparation of an alkyliodosilane. Eaborn[2] described the preparation of alkyliodosilanes by the cleavage of tetraalkylsilanes with aluminum iodide and iodine. Deans and Eaborn[3] recently studied the kinetics of the reaction of trialkylsilanes with iodine.

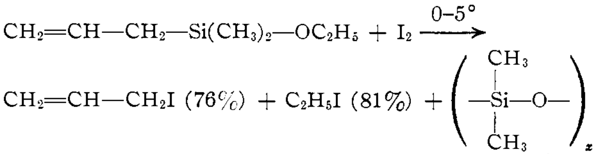
Sommer, Tyler and Whitmore[4] described the addition of chlorine, hydrogen bromide and hydrogen iodide to the double bond of allyltrimethylsilane and the cleavage of the allyl–silicon bond in allyltrimethylsilane by bromine, hydrogen chloride and sulfuric acid. They postulated a carbonium ion (I) intermediate as common to both reactions. Electron-release from silicon to the electronically deficient β-carbon with simultaneous or subsequent union of the resulting "siliconium ion" with the negative part of the attacking reagent was proposed as the mechanism of the cleavage reaction.

$$(CH_3)_3SiCH_2CH{=}CH_2 \xrightarrow{A^+B^-} \underset{\text{I}}{(CH_3)_3SiCH_2\overset{+}{C}HCH_2A} \quad (1)$$



$$(CH_3)_3Si\text{—}CH_2\text{—}\overset{+}{C}HCH_2A + \mathbf{B}^- \longrightarrow (CH_3)_3SiB + CH_2{=}CHCH_2A \quad (2)$$

This paper reports the vigorous exothermic reaction of iodine and allylsilanes at room temperature. More surprising, however, was the discovery that when the allylsilane has an ethoxy group attached to the silicon atom, ethyl iodide and a polymer are produced even at 0°, in addition to allyl iodide. No iodosilane was isolated. Thus with allylethoxydimethylsilane



$$CH_2{=}CH\text{—}CH_2\text{—}Si(CH_3)_2\text{—}OC_2H_5 + I_2 \xrightarrow{0\text{–}5°} CH_2{=}CH\text{—}CH_2I\ (76\%) + C_2H_5I\ (81\%) + \left(\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\right)_x \quad (3)$$

In Table I are listed the compounds studied and the yields of iodosilane, allylic iodide and ethyl iodide observed. In addition to the compounds listed, qualitative test-tube experiments showed that iodine reacted violently with diallyldiethoxysilane but did not react with diethoxymethylphenylsilane, diethoxydimethylsilane, ethyl silicate and *m*-trifluoromethylbenzyltrimethylsilane.[5]

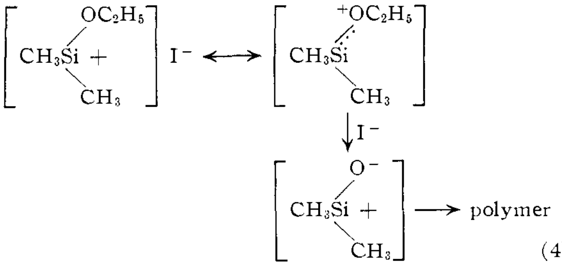
TABLE I

CLEAVAGE OF ALLYLSILANES BY IODINE

Silane	Yield, % Allyl iodide	Ethyl iodide	Iodo-silane
Allylethoxydimethyl-	76	81	0
Allyldiethoxymethyl-	67	77[a]	0
Allyldiethoxyphenyl-	67	88[a]	0
	65	90[a]	0
"Methallyltriethoxy-[b]"	[c]	49[a]	. .
Allyltrimethyl-	Quant.[d]	. .	Quant.[d]

[a] Assuming only one ethoxy group/molecule available. [b] Prepared by C. E. Arntzen from the reaction of methallyl chloride, magnesium and ethyl silicate; $n^{25}D$ 1.4109, d^{25} 0.8999, b.p. 102.5° (40 mm.); MR_D obsd. 60.27, MR_D calcd. 59.87. Infrared spectrum indicates crotyl structure. [c] Not isolated. [d] Isolated as the minimum boiling azeotrope of allyl iodide and hexamethyldisiloxane, b.p. 95° (740 mm.). Composition of azeotrope is approximately 48% hexamethyldisiloxane, 52% allyl iodide as determined from plot of specific volume *vs*. composition.

Since iodine does not normally cleave alkyl–oxygen bonds, it seems necessary to postulate an electronic interaction between the ether oxygen and the electron-deficient silicon atom in order to account for the cleavage as well as the failure to isolate an ethoxyiodosilane. Such an interaction would facilitate the nucleophilic displacement by iodide or iodine on carbon. Thus, expanding the Sommer–Whitmore mechanism leads to the attractive possibility of a silicon-oxygen "polar" or double bond as a transient intermediate:



(4)

An alternative mechanism is suggested by the work of Kumada,[6] who reported the cleavage of some ethoxysilanes by bromotrimethylsilane at elevated temperatures in the presence of pyridine

---

[1] B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. Di Giorgio and F. C. Whitmore, THIS JOURNAL, **70**, 433 (1948).

[2] C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

[3] D. K. Deans and C. Eaborn, *ibid.*, 3169 (1954).

[4] L. H. Sommer, L. J. Tyler and F. C. Whitmore, THIS JOURNAL, **70**, 2872 (1948).

[5] Prepared by L. W. Frost, to be described later.

[6] M. Kumada and H. Hattori, *J. Inst. Polytech., Osaka City U.*, **3**, 77 (1952).