with alkali,[12] with adoption of the most stable arrangement, like that of ε-truxillic acid, having no *cis* adjacent groups, by the failure to cyclize δ-truxinic acid to a hydrindone,[2] and by Hofmann degradation and deamination.[13] Since in base an amide group should form an enolate more readily than does a carboxylate ion, selective inversion of the amide portion of an amido acid would be anticipated, and has been demonstrated for the transformations of β-truxinamic to *neo*-a-truxinamic[4] and of *peri*-truxillamic to *epi*-b-truxillamic[6] acid. Inversion of the amide group of VII gives formula IV for the ζ-b-derivatives.[14]

(12) The reported isomerization[1] of β- to δ-truxinic acid by concentrated hydrochloric acid during six hours at 160° would represent a unique inversion of a phenyl substituent in *acid*. The change seems questionable, however, for a subsequent publication (R. Stoermer and F. Bachér, *Ber.*, **55**, 1860 (1922)) described the conversion of *neo*-truxinic acid by concentrated hydrochloric acid during four hours at 170–180° to a mixture that melted higher than the δ-acid and contained the β-acid.

(13) R. Stoermer and E. Asbrand, *ibid.*, **64**, 2793 (1931).

(14) Base-catalyzed isomerization of an a-half ester of I would lead to a new truxinic acid. The so-called μ- and ω-truxinic acids of M. M. Shemiakin (*Compt. rend. acad. sci. U.R.S.S.*, **24**, 768 (1939); **29**, 199, 202 (1940); [*Brit. Chem. Physiol. Abstr.*, **AII**, 169 (1941)]; *Zhur. Obshchei Khim.*, **11**, 219 (1941); [*C. A.*, **35**, 7944 (1941)]) appear to be lactonic acids.

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Steric Effects in Grignard Couplings with Alkoxysilanes[1]

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Some years ago we described[3] a general method for the preparation of difficultly accessible trialkylsilyl compounds which involved the reaction of alkyl Grignard reagents with ethyl orthosilicate. The utility of this type of synthesis is evidenced by

$$\text{RMgX} + (\text{EtO})_4\text{Si} \longrightarrow \text{R}_3\text{SiOEt}$$

the frequent use which has been made of it.[4] The success of the method depends on the fact that in general only three of the ethoxy groups of ethyl orthosilicate are replaced by alkyl Grignard reagents even under forcing conditions. For this reason an excess of Grignard reagent may be used to drive the reaction to the formation of a good yield of the trisubstituted derivative[5] without fear of over-stepping to the formation of by-product tetra-alkylsilane.[6,7] We now wish to report a more detailed investigation completed shortly after our earlier work,[3] which suggests that steric factors[8] play an important role in stopping the substitution at the desired stage.

In delineating the scope of the reaction we have found that ethyl and *n*-propyl Grignard reagents do not replace the fourth ethoxy group of ethyl orthosilicate even when a large excess of the organometallic compound is used and the reaction mixture is heated at 100°.[9] On the other hand methyl and phenyl Grignard reagents readily replace the fourth ethoxy group, giving tetramethylsilane and tetraphenylsilane respectively.[10] That this behavior is dependent more upon steric factors than upon Grignard reactivity or polar factors is suggested by the aforementioned results coupled with the following observations. Phenylmagnesium bromide does not replace the ethoxy group of triethylethoxysilane even under forcing conditions. Yet *n*-propylmagnesium bromide replaces the ethoxy group of trimethylethoxysilane with formation of *n*-propyltrimethylsilane.[11]

Experimental

Grignard Reagents with Ethyl Orthosilicate. A. Methylmagnesium bromide.—The Grignard reagent was prepared in the usual manner from 525 g., 21 moles, of magnesium turnings, 1.5 liters of liquid methyl bromide and seven liters of anhydrous ether. To the solution of organometallic reagent was added in thirty-five minutes with stirring and tap water cooling 1460 g., 7.0 moles, of ethyl orthosilicate.[12] Upon standing the reaction mixture separated into two layers, the lower of which solidified during the night. Fractional distillation of the seven-liter upper layer gave an ether fraction b. 25–35°, containing about two moles, 30% yield,

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(1) Paper 49 in a series on organosilicon chemistry. For the preceding paper see THIS JOURNAL, **77**, 2485 (1955).

(2) Deceased, 1947.

(3) P. D. George, W. A. Strong, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 1380 (1946).

(4) No complete record has been kept but the following references are representative: (a) L. H. Sommer, D. L. Bailey, R. E. Van Strien and F. C. Whitmore, paper presented before the 109th American Chemical Society Meeting in April, 1946; (b) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946); (c) H. Gilman and F. J. Marshal, *ibid.*, **71**, 2066 (1949); (d) N. S. Marans, L. H. Sommer and F. C. Whitmore, *ibid.*, **73**, 5127 (1951); (e) E. Larsson and R. Marin, *Acta Chem. Scand.*, **5**, 1173 (1951); (f) A. D. Petrov and L. L. Shchukoskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 564–565, 1952; (g) E. Larsson, *K. Fysiogr. Sällskap. Lund, Förh. (Lund)*, **22**, No. 15, 1–4 (1952).

(5) Poor yields of trialkylsilyl derivatives are obtained upon coupling Grignard reagents with silicon tetrachloride: see for example C. R. Noller and H. W. Post. THIS JOURNAL, **74**, 1361 (1952).

(6) The preparation of tetra-*n*-butylsilane from the reaction of *n*-butylmagnesium bromide and ethyl orthosilicate under forcing conditions was erroneously reported by H. W. Post and C. H. Hofrichter, *J. Org. Chem.*, **5**, 572 (1940). Their product was probably Bu_3SiOEt—see P. D. George, Doctoral Dissertation, Pennsylvania State University, 1946; R. O. Sauer, THIS JOURNAL, **68**, 954 (1946); H. Gilman and R. N. Clark, *ibid.*, **69**, 967 (1947).

(7) Organolithium reagents are apparently much more reactive toward ethyl orthosilicate for they readily give symmetrical and unsymmetrical tetra-alkylsilanes: see H. Gilman and R. N. Clark, *ibid.*, **68**, 1675 (1946); H. Gilman and F. J. Marshall, *ibid.*, **71**, 2066 (1949); M. G. Voronkov, B. N. Dolgov and N. P. Zapevalova, *Uchenye Zapiski, Leningrad. Gosundarst. Univ.* No. **163**, Ser. Khim. Nauk No. 12, 161–176 (1953); *C. A.*, **49**, 5272*g* (1955).

(8) The role of steric factors in other reactions involving substitution at a silicon atom have been demonstrated repeatedly. For leading references see H. Gilman and C. G. Brannen, THIS JOURNAL, **73**, 4640 (1951). More recent references include: C. Eaborn, *J. Chem. Soc.*, 2840 (1952); H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **19**, 441 (1954); L. H. Sommer and L. J. Tyler, THIS JOURNAL, **76**, 1030 (1954); L. H. Sommer, R. M. Murch and F. A. Mitch, *ibid.*, **76**, 1619 (1954).

(9) Findings have been reported recently which confirm these results and extend them to higher alkyl Grignard reagents: E. Larsson, *Kgl. Fysiograph. Sällskap. Lund, Handl.*, **63**, No. 12, 1–8 (1952).

(10) Another Grignard reagent recently reported to form a tetraorganosilane from ethyl orthosilicate is 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide: E. T. McBee, C. W. Roberts, G. F. Judd and T. S. Chao, THIS JOURNAL, **77**, 1292 (1955).

(11) Related studies involving competitive reactions of Grignard reagents with trialkylmonochlorosilanes have been described: L. H. Sommer, G. T. Kerr and F. C. Whitmore, THIS JOURNAL, **70**, 434 (1948).

(12) The ethyl orthosilicate used in this work was a technical grade purchased from Carbide and Carbon Chemical Corp. Careful fractional distillation of a random sample showed that it contained substantially no ethanol or siloxane polymers. Well over 90% of the material was ethyl silicate which had b.p. 164–164.8° at 725 mm., $n^{20}\text{D}$ 1.3838, d^{20} 0.9336, and η^{22} 0.762 centistokes.

of tetramethylsilane,[13,14] which was identified by its insolubility in concentrated sulfuric acid and its $n^{20}\mathrm{D}$ 1.3600. From the solid residue there was obtained by the procedure previously described[15] a 55% yield of hexamethyldisiloxane.

B. **Ethylmagnesium Bromide.**—Since our earlier work[3] it has been demonstrated that even under forcing conditions and with an excess of Grignard reagent neither ethyl magnesium bromide[16] nor ethylmagnesium chloride[4g,9] give tetraethylsilane upon reaction with ethyl orthosilicate.

C. ***n*-Propylmagnesium Bromide.**—The Grignard reagent was prepared in the usual manner from 4 moles of magnesium turnings, 4 moles of *n*-propyl bromide, and 1 liter of anhydrous ether.

To the Grignard reagent was added with stirring at reflux temperature over a period of one and one-half hours 160 g., 0.77 mole, of ethyl orthosilicate. The refluxing subsided shortly after the addition was completed. After being stirred at room temperature for sixteen hours, the reaction mixture was heated to reflux for twenty hours; then the ether was removed by distillation.

The residue was hydrolyzed by pouring onto ice, and then the mixture was modified with hydrochloric acid. The organic layer, combined with ether extracts of the aqueous layer, was freed of ether by distillation. The resulting residue was washed thoroughly with concentrated sulfuric acid and then with water. Dilution of the acid wash with water gave only 8 g. of dark, viscous oil. The washed, crude product was dried over a mixture of anhydrous calcium chloride and potassium carbonate. Distillation of the resulting 85 g. of material gave 60 g., 0.18 mole, 47% yield of hexa-*n*-propyldisiloxane,[17] b. 284–287° at 737 mm., $n^{20}\mathrm{D}$ 1.4410–3. The reaction was successfully repeated,[18] giving a 48% yield of material, b.p. 242–243° at 260–270 mm., $n^{20}\mathrm{D}$ 1.4410, d^{20} 0.8361.

The disiloxane was converted to the corresponding monochloride by the method of Flood.[19] Hexa-*n*-propyldisiloxane, 67 g., 0.20 mole, was mixed with 75 ml. of concentrated sulfuric acid. To the wine-colored mixture was added slowly with vigorous agitation 53 g. of ammonium chloride. There was considerable frothing but no rise in temperature. About half way through the addition 50 ml. more of concentrated sulfuric acid was added to the reaction mixture. When the addition was complete, stirring was continued for one-half hour, and then the reaction mixture was allowed to stand overnight open to the atmosphere through a drying tube. A 73 g., wine-colored, upper layer was separated from the clear, viscous, lower layer, which was discarded. Distillation of the crude product gave 54 g., 0.28 mole, 70% yield of tri-*n*-propylchlorosilane,[17,20,21] b.p. 197–200° at 737 mm. $n^{20}\mathrm{D}$ 1.4404. The reaction was successfully repeated[18] and the product was converted to tri-*n*-propylsilylamine.

D. **Phenylmagnesium Bromide.**—The Grignard reagent was prepared in the usual manner from 4 moles of magnesium turnings, 4 moles of bromobenzene, and 1 liter of dry ether. To the Grignard reagent was added with stirring at reflux temperature 150 g., 0.72 mole, of ethyl orthosilicate. The reaction mixture was stirred for one hour, the ether was removed by distillation, and the resulting residue was heated for ten hours on the steam-bath. Hydrolysis and acidification with hydrochloric acid was followed by steam distillation until no more organic material appeared in the distillate. The solid remaining in the aqueous residue from the steam distillation was filtered and washed with acetone to remove triphenylsilanol. Only 3 g. of unidentified material which melted above 200°, was obtained by evaporating the acetone wash. The crude, solid product was extracted repeatedly with a one-liter portion of boiling benzene from which crystals precipitated on cooling after each extraction. Finally there remained only 8 g. of insoluble gray putty-like material, which was discarded. The combined crops weighed 140 g. and melted at 231–233°. Evaporation of the mother liquor from the final extraction and crystallization gave another crop which, after one recrystallization, weighed 5 g. and melted at 233–234°. The yield of tetraphenylsilane[22] was 60%; in other runs the yields were 29 and 43%, respectively.[23] The recrystallized product, m.p. 233–234°, gave no freezing point depression with authentic tetraphenylsilane, m.p. 234°, made in 46% yield from the Grignard reagent and silicon tetrachloride.[24]

Tetraphenylsilane from both sources had the following crystal properties according to Dr. Mary L. Willard of this Laboratory. The compound crystallized from benzene in clear, colorless, bladed needles most of which were wedge-shaped. Some showed 90° silhouette angles, and others were pyramidal with an acute silhouette angle of about 35°. Most of the crystals were oriented so that a positive, acute, bisectrix figure was obtained. The optic axial angle was 40°. The bladed needles were length-fast, making the most commonly presented face (also the B_{x_a} face) the 100 face. The optic axial plane was parallel to the 010 face. The crystals all showed parallel extinction, they belonged to the orthorhombic systems, and gave the following refractive indexes: $\alpha = 1.674, \beta = 1.725$, and $\gamma = 1.850$.

Triethylethoxysilane with Phenylmagnesium Bromide.—Crude triethylethoxysilane was prepared from the reaction of 145 g., 0.69 mole, of ethyl orthosilicate with ethylmagnesium bromide made from 97 g., 4.0 moles, of magnesium turnings, 450 g., 4.1 moles, of purified ethyl bromide and one liter of anhydrous ether. The reaction mixture was freed of ether and the residue was heated on a steam-bath for eight hours. Returning 400 ml. of the ether rendered fluid the residue containing crude triethylethoxysilane, and it was added to phenylmagnesium bromide made from 36 g., 1.5 moles, of magnesium turnings, 240 g., 1.5 moles, of purified bromobenzene, 400 ml. of ether and 300 ml. of benzene. The solvents were removed from the reaction mixture and the residue was heated for sixteen hours on a steam-bath. Hydrolysis with dilute hydrochloric acid and fractional distillation of the organic material gave 42 g. boiling in the expected product range. This material boiled at 231–235° and had $n^{20}\mathrm{D}$ 1.4440–1.4576. Upon being chilled to 0° it deposited 2 g. of crystals which were identified as biphenyl, m.p. 68–69° after recrystallization from methanol. The major product then had $n^{20}\mathrm{D}$ 1.4460, and was readily and completely soluble in cold concentrated sulfuric acid. It probably consisted mainly of hexaethyldisiloxane, b.p. 233°, $n^{20}\mathrm{D}$ 1.4340. No phenyltriethylsilane[25] (b.p. 237°, $n^{26}\mathrm{D}$ 1.4990) was found and no more than a very small amount could have been formed.[26,27]

Trimethylethoxysilane with *n*-Propylmagnesium Bromide.—To 440 ml. of 3.3 molar *n*-propylmagnesium bromide in ether was added 100 g., 0.85 mole, of trimethylethoxysilane. The reaction mixture was refluxed 24 hours and freed of ether through an efficient distillation column to prevent loss of volatile starting material. The residue was heated 72 hours on the steam-bath and then cautiously hydrolyzed with dilute hydrochloric acid to prevent loss of volatile

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[13] A. Bygden, *Ber.*, **44**, 2640 (1911).

[14] M. Kumata and K. Tarama, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **54**, 213–215 (1951) (*C. A.*, **47**, 2581*d* (1953)), also obtained a "substantial amount" of tetramethylsilane from the reaction of 4 moles of MeMgCl with 1 mole of $(EtO)_4Si$ in ether at reflux temperature. In reference (9) there was obtained from the same reaction a 76% yield of Me_3SiOEt; no tetramethylsilane was reported.

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

[16] N. S. Marans, L. H. Sommer and F. C. Whitmore, *ibid.*, **73**, 5127 (1951).

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

[18] R. E. Van Strien, M.S. Thesis, Pennsylvania State University, 1944.

[19] E. A. Flood, THIS JOURNAL, **55**, 1735 (1933).

[20] M. G. Voronkov, B. N. Dolgov and N. A. Dmitrieva, *Doklady Akad. Nauk, SSSR*, **84**, 959–961 (1952); *C. A.*, **47**, 3228*d* (1953).

[21] H. Breederveld and H. I. Waterman, *Research Correspondence*, **6**, 145–155 (1953).

[22] A. Polis, *Ber.*, **18**, 1540 (1885).

[23] The isolation of 3–5% yields of Ph_4Si from reaction of PhMgBr with $(EtO)_4Si$ has been reported: A. V. Topchiev and N. S. Nametkin, *Doklady Akad. Nauk, SSSR*, **80**, 897–898 (1951); *C. A.*, **46**, 7534*d* (1952).

[24] N. W. Cusa and F. S. Kipping, *J. Chem. Soc.*, 1040 (1933).

[25] R. N. Meals, THIS JOURNAL, **68**, 1880 (1946).

[26] W. A. Strong, Doctoral Dissertation, Pennsylvania State University, 1944, *obtained similar results with purified triethylethoxysilane*; much of the starting material was recovered and no phenyltriethylsilane was found. On the other hand triethylchlorosilane with phenylmagnesium bromide gave a 60% crude yield of phenyltriethylsilane.

[27] A small amount of Me_2SiPh_2 was obtained when a reaction mixture consisting of 2.0 moles of chlorobenzene, 2.3 moles of $Me_2Si(OEt)$ and 2.0 atoms of magnesium was refluxed for ten hours: W. H. Daudt and J. F. Hyde, THIS JOURNAL, **74**, 386 (1952).

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.

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[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 $Me_2Si(OEt)_2$ with excess *n*-PrMgCl under forcing conditions were $MePr_2SiOEt$ and $Me_2PrSiOEt$, respectively; however, small amounts of $MeSiPr_3$ and Me_2SiPr_2 also were obtained.

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

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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

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[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).