and phenyl benzenethiolsulfonate were obtained. This glc disproportionation behavior was confirmed with an authentic sample of phenyl benzenethiolsulfinate.

Acknowledgment.—We thank the Air Pollution Control Office of the Environmental Protection Agency (Grant AP 00925) and the National Science Foundation (Grant 29373X) for support of this work. We also acknowledge helpful discussions with Dr. Eric Block, and thank Mrs. Anjali Jindal for assistance with some of the experiments.

The Preparation and Reactions of Novel *O*-Acylhydroxylamines

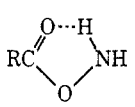
WILLIAM N. MARMER*[1a] AND GERHARD MAERKER

Eastern Regional Research Laboratory,[1b] Philadelphia, Pennsylvania 19118

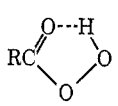
Received March 17, 1972

The new compounds *O*-pivaloyl-, *O*-(*p*-nitrobenzoyl)-, and *O*-(*m*-chlorobenzoyl)hydroxylamine as well as the previously prepared *O*-acetyl-, *O*-benzoyl-, and *O*-mesitoylhydroxylamines have been prepared in order to study their behavior with various nucleophiles. Because of the propensity of most *O*-acylhydroxylamines to isomerize to hydroxamic acids, attention was given to the bulky *O*-pivaloyl and *O*-mesitoyl compounds. *O*-Pivaloylhydroxylamine does transfer nitrogen to iodide ion (product is iodine), dibenzylamine (product is *N*,*N*-dibenzylhydrazine), and triphenylphosphine (product is iminotriphenylphosphorane). Nevertheless, olefins fail to react in the presence of *O*-acylhydroxylamines. Preferential isomerization of the *O*-acyl compounds to the corresponding hydroxamic acids occurs even when the highly substituted tetramethylethylene is treated with the bulky *O*-pivaloylhydroxylamine. Although *O*-mesitoylhydroxylamine does not isomerize, it decomposes to mesitoic acid when heated with or without an olefin (*cis*-3-hexene).

In an effort to develop a new and economical method for preparating N-unsubstituted aziridines from olefins, a study has been undertaken of the ability of *O*-acylhydroxylamines[1c] to transfer nitrogen. *O*-Acylhydroxylamines (**1**) are nitrogenous analogs of organic peracids (**2**) and, like the latter, have the potential to react with various nucleophilic regents. Nevertheless, there are surprisingly few reports of nucleophilic reactions on *O*-acylhydroxylamines and, indeed, few *O*-acylhydroxylamines have even been prepared and characterized.



1



2

There is only a meager amount of literature citing the attack of nucleophiles upon *O*-acylhydroxylamines. Treatment with potassium iodide liberates iodine (eq 1).[2] Also documented are the reactions of

$$1 + I^- \xrightarrow{H_2O} RCO_2H + [H_2NI] \xrightarrow{I^-,\ H_2O} NH_3 + I_2 \quad (1)$$

O-mesitoylhydroxylamine [*O*-(2,4,6-trimethylbenzoyl)-hydroxylamine] with secondary amines to give hydrazides,[3] and with sulfonamides to give sulfohydrazides.[4] *O*-acylhydroxylamines are known to rearrange to the thermodynamically more stable *N*-acyl compounds, hydroxamic acids. Since Jencks has found[5] that hydroxylamine often is acylated at the oxygen end of the molecule, this rearrangement must be at least partly responsible for the finding that direct acylation gives only the hydroxamic acid as an isolable entity. In order to minimize the isomerization of *O*-acylhydroxylamines, the carbonyl group must be protected by sufficient bulk in its vicinity. Carpino has shown[3] that such stability is imparted by a mesityl group. In the present work the *tert*-butyl group was relied upon to provide similar stability to the product.

Results and Discussion

If hydroxylamine is acylated initially upon its oxygen, and if the *tert*-butyl group provides the necessary stability to the O-acylated material, then treatment of hydroxylamine with pivaloyl chloride (trimethylacetyl chloride) should constitute a simple, direct procedure for the synthesis and isolation of *O*-pivaloylhydroxylamine. Although the *tert*-butyl group does provide some stability toward isomerization (see below), the reaction of pivaloyl chloride with hydroxylamine gave the *N*-pivaloylhydroxylamine (pivalohydroxamic acid) as the only product. Since the direct synthesis appeared inadequate, indirect methods were necessary.

The two procedures[6,7] that we followed to obtain new *O*-acylhydroxylamines both relied on initial addition of a blocking group upon the nitrogen of hydroxylamine, then O-acylation, and finally removal of the nitrogen block. For this study the known compounds *O*-benzoyl- and *O*-mesitoylhydroxylamine were prepared, as well as the new compounds *O*-pivaloyl-, *O*-(4-nitrobenzoyl)-, and *O*-(3-chlorobenzoyl)hydroxylamine. A variety of new compounds classified as intermediates in the synthetic procedures were also synthesized.[8]

We found that both the new and the reported "bulky" *O*-acylhydroxylamines do in fact suffer some decomposition. Solutions of *O*-pivaloylhydroxylamine in chloroform are stable at room temperature for longer than 1 month, but the neat free base does isomerize to pivalohydroxamic acid within hours at room temperature and over Dry Ice within 1 week. We found that *O*-mesitoylhydroxylamine has a tendency to revert to the carboxylic acid upon heating.

(1) (a) National Research Council–Agricultural Research Service Postdoctoral Research Associate, 1970–1972; (b) Eastern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture; (c) for brevity, the term "acyl" is to be taken to include various "aroyl" groups as well.

(2) (a) G. Zinner, *Angew. Chem.*, **72**, 76 (1960); (b) P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *J. Amer. Chem. Soc.*, **86**, 1139 (1964).

(3) L. A. Carpino, *ibid.*, **82**, 3133 (1960).

(4) L. A. Carpino, *J. Org. Chem.*, **30**, 321 (1965).

(5) W. P. Jencks, *J. Amer. Chem. Soc.*, **80**, 4581, 4584 (1958).

(6) L. A. Carpino, C. A. Giza, and B. A. Carpino, *ibid.*, **81**, 955 (1959).

(7) G. Zinner, *Arch. Pharm. (Weinheim)*, **293**, 657 (1960).

(8) Attempts to carry some of these compounds through to *O*-acylhydroxylamines failed.

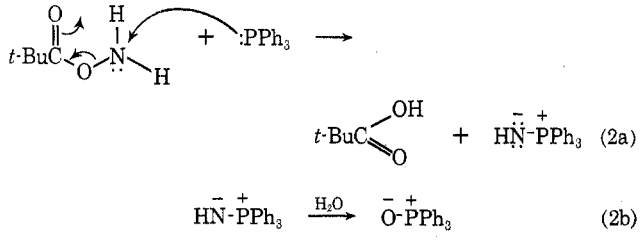
The hydrochloride salts of *O*-acylhydroxylamines are considerably more stable than the free bases. We have ascertained by differential scanning calorimetry that solid *O*-pivaloylhydroxylamine hydrochloride is stable below 127° (and *O*-benzoylhydroxylamine hydrochloride below 73°).

Nitrogen Transfer Reactions.—*O*-Acylhydroxylamines, like their peracid analogs, are expected to show some reactivity as both nucleophiles and electrophiles. As nucleophiles, the amino groups of the *O*-acylhydroxylamines should behave as *hard* bases. *O*-Acylhydroxylamines demonstrate this property both in their ease of salt formation and in their reaction with ketones to form *O*-acyl oximes. Indeed, oxime formation was used to demonstrate proof of structure of *O*-pivaloylhydroxylamine. The product isolated from treatment of the *O*-acylhydroxylamine with cyclohexanone was identical with the compound obtained by treatment of cyclohexanone oxime with pivaloyl chloride. As electrophiles, the electron-deficient amino groups should undergo nucleophilic attack by soft bases. In this process, nitrogen should be transferred to the nucleophile. There is a wide range of reactivity among soft-base nucleophiles; we have chosen for reaction upon *O*-pivaloylhydroxylamine two "potent" nucleophiles (iodide ion and triphenylphosphine), an "average" one (dibenzylamine), and a "reluctant" type (compounds with olefinic bonds).

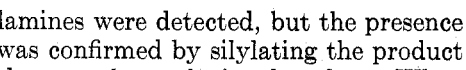
The *O*-acylhydroxylamines prepared in the current work reacted with iodide, thus confirming the results achieved by previous workers.[2] The reaction with iodide was used to obtain a qualitative (starch–iodide test) as well as quantitative (iodometric) measure of the amounts of *O*-acylhydroxylamines.

Triphenylphosphine, regarded as a potent soft-base nucleophile, has been reported to attack chloramine and also hydroxylamine-*O*-sulfonic acid, two analogs of *O*-acylhydroxylamines. In both cases, the expected product, iminotriphenylphosphorane ($^+Ph_3P$–NH^-), rapidly hydrolyzed to triphenylphosphine oxide ($^+Ph_3P$–O^-). Isolation of the intermediate was feasible only when the reaction was carried out in liquid ammonia.[9]

We have found that neat *O*-pivaloylhydroxylamine reacts violently with triphenylphosphine, with tri-*n*-butylphosphine, and with methyl phosphite, but the rate of reaction may be controlled by using carbon tetrachloride as a solvent. A 78% yield of triphenylphosphine oxide was obtained from the moderated reaction (eq 2). In the final mixture, no *O*-acyl- and



(2a)



(2b)

N-acylhydroxylamines were detected, but the presence of pivalic acid was confirmed by silylating the product mixture and subsequently analyzing by glpc. When the reaction was carried out under acidic conditions, the P–N compound was isolated as an acid salt. *O*-Pivaloylhydroxylamine hydrochloride reacted with triphenylphosphine in absolute methanol to give iminotriphenylphosphorane hydrochloride.

We have shown that *O*-pivaloylhydroxylamine can transfer nitrogen to dibenzylamine (eq 3). When

$$(CH_3)_3CCO_2NH_2 + NHBz_2 \longrightarrow (CH_3)_3CCO_2H + H_2NNBz_2 \quad (3)$$

the reaction was carried out on a 1:1 molar mixture without cosolvent, it was complete at 100° within 1 min, no *O*-acylhydroxylamine remained, and no isomerization product was present. *N*,*N*-Dibenzylhydrazine was isolated as its benzaldehyde hydrazone in 14% yield. Similar results were obtained in reactions run in nitromethane or in chloroform. Nmr analysis of a reaction carried out in deuteriochloroform (molar ratio of *O*-pivaloylhydroxylamine:dibenzylamine 1:5; 78°, 16 hr) suggested a quantitative conversion of amine to hydrazine.

Despite the affinity of the aforementioned nucleophiles for *O*-acylhydroxylamines, no evidence for the direct reaction of olefins with *O*-acylhydroxylamines could be detected. In general, *O*-acylhydroxylamines merely isomerized to the corresponding hydroxamic acids, while the olefins remained intact. Such results were obtained with *O*-(3-chlorobenzoyl)hydroxylamine, *O*-benzoylhydroxylamine, *O*-(4-nitrobenzoyl)-hydroxylamine, and even with the bulky *O*-pivaloylhydroxylamine. The olefins tested included *cis*-3-hexene, *cis*-5-decene, 2,3-dimethyl-2-butene, and 2,3-dimethyl-2-hexene. Occasionally, cosolvents such as benzene or methylene chloride were used.

O-Mesitoylhydroxylamine, unlike the other *O*-acylhydroxylamines, did not isomerize on heating with an olefin (*cis*-3-hexene). Although a good yield of mesitoic acid was obtained, there was no evidence for any nitrogen transfer to the olefin. Determination of the fate of the N fragment awaits further study.

Experimental Section

Nmr spectra were produced on a Jeolco C-60H[10] instrument. Chemical shifts are relative to internal tetramethylsilane. Differential scanning calorimetry experiments utilized a Perkin-Elmer DSC-IB instrument. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Thin layer chromatography utilized Eastman chromagram silica gel sheets with fluorescent indicator. Spots were visualized under uv light and after treatment with iodine vapor. Infrared spectra were obtained on a Perkin-Elmer Model 237B grating infrared spectrophotometer.

Synthesis of *tert*-Butyl *N*-Hydroxycarbamate (3) ($HONHCO_2$-*t*-Bu).—The method of Carpino[6] was used to synthesize **3** from *tert*-butoxycarbonyl azide (Aldrich, used as received) and hydroxylamine, yield 75% from Cellosolve B–methylene chloride, mp 55.5–57° (lit.[6] mp 55–57.5°).

Synthesis of *tert*-Butyl *N*-Acyloxycarbamates (4) (RCO_2-$NHCO_2$-*t*-Bu).—Continuation of Carpino's method[6] gave the following new compounds.

A. *tert*-Butyl *N*-Pivaloyloxycarbamate (4, R = *tert*-Butyl).—Pivaloyl chloride (Eastman) was distilled prior to use, and reacted with **3** to give an 87% yield of product, mp 77–78°, from Cellosolve B. *Anal.* Calcd for $C_{10}H_{19}NO_4$: C, 55.28; H, 8.81; N, 6.45. Found: C, 55.68; H, 8.85; N, 6.20.

B. *tert*-Butyl *N*-(4-Nitrobenzoyloxy)carbamate (4, R = 4-$NO_2C_6H_4$).—4-Nitrobenzoyl chloride (Eastman) was recrystal-

(9) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, pp 217–218.

(10) Reference to a particular manufactured product does not constitute a recommendation by the U. S. Department of Agriculture over similar products not mentioned.

lized prior to use, and reacted with **3** to give a 94% yield of product from Cellosolve B–benzene, mp 93–94°. *Anal.* Calcd for $C_{12}H_{14}N_2O_6$: C, 51.06; H, 5.00; N, 9.92. Found: C, 51.66; H, 6.27; N, 9.57.

C. *tert*-Butyl *N*-(3-Chlorobenzoyloxy)carbamate (4, R = 3-ClC_6H_4).—3-Chlorobenzoyl chloride was prepared from 3-chlorobenzoic acid and oxalyl chloride, according to the method of Bosshard, *et al.*[11] A short-path distillation gave a 71% yield of the product, bp 80–90° (10 Torr) [lit.[12] bp 104–106° (14 Torr)]. Treatment with **4** gave a viscous, yellow oil (crude yield 99%). The oil was used in the synthesis of the *O*-aroylhydroxylamine without further purification.

D. *tert*-Butyl *N*-benzoyloxycarbamate (4, R = C_6H_5) was obtained in 89% yield recrystallized from hexane, mp 81–83° (lit.[6] mp 82–84°).

E. *tert*-Butyl *N*-mesitoyloxycarbamate (4, R = 2,4,6-$(CH_3)_3C_6H_2$) was obtained in 85% yield from Cellosolve B, mp 75–76° (lit.[3] mp 78–79.5°).

Synthesis of Ethyl *N*-Hydroxyacetimidate (5) [$CH_3C(OEt)$=NOH].—This oxime derivative of ethyl acetate was synthesized in 14% yield from ethyl acetimidate, according to the method of Houben and Schmidt.[13] The product solidified as needles: mp 25–26° after distillation; bp 54.5° (9 Torr); nmr (CCl_4) δ 1.25 (t, 3 H, CH_3 of ethyl), 1.9 (s, 3 H, CH_3C=N), 3.85 (q, 2 H, CH_2 of ethyl), 8.3 (s, 1 H, HON=C).

Synthesis of Ethyl *N*-Acyloxyacetimidates (6) [$CH_3C(OEt)$=NOCOR].—The following compounds were synthesized according to the Zinner procedure.[7]

A. Ethyl *N*-Pivaloyloxyacetimidate (6, R = *tert*-Butyl).—Treatment of **5** with pivaloyl chloride (Eastman, distilled) gave a 79% crude yield of product, 69% distilled yield, bp 38–39° (0.10 Torr), 60.5° (1.0 Torr). The sample was too unstable to result in a suitable element analysis. Nmr (CCl_4) δ 1.2 [s, $(CH_3)_3C$] and 1.3 (t, CH_3 of ethyl), sum of areas 11 H, 1.9 (s, 4 H, CH_3C=N) (impurity at baseline), 4.1 (q, 2 H, CH_2 of ethyl).

B. Ethyl *N*-(2,5-Dichlorobenzoyloxy)acetimidate (6, R = 2,5-$Cl_2C_6H_3$).—**5** was aroylated with 2,5-dichlorobenzoyl chloride (Hooker Chemical Co., Industrial Chemical Division; material used without further work-up): crude yield 63%; mp 58–68° from petroleum ether; recrystallized yield 32% from ether; very large, glassy crystals; mp 69.5–71.0°. *Anal.* Calcd for $C_{11}H_{11}NCl_2O_3$: C, 47.85; H, 4.02; N, 5.07; Cl, 25.68. Found: C, 48.24; H, 4.18; N, 5.04; Cl, 25.58. Nmr ($CDCl_3$) δ 1.3 (t, 3 H, CH_3 of ethyl), 2.1 (s, 3 H, CH_3C=N), 7.3 (m, 2 H, meta and para H's), 7.7 (m, 1 H, ortho H), 4.2 (q, 2 H, CH_2 of ethyl).

C. Ethyl *N*-Trifluoroacetoxyacetimidate (6, R = CF_3).—Trifluoroacetylation of **5** with trifluoroacetic anhydride (Eastman, used as received) and pyridine gave a crude yield (oil with fruity odor) of 93%: distilled yield 70%; bp 41° (10 Torr); nmr (CCl_4) δ 1.3 (t, 3 H, CH_3 of ethyl), 2.05 (s, 3 H, CH_3C=N), 4.15 (q, 2 H, CH_2 of ethyl).

D. Synthesis of Ethyl *N*-Methanesulfonoxyacetimidate [CH_3SO_2ON=$C(CH_3)OC_2H_5$].—This sulfonyl analog of **6** was prepared from **5** and methanesulfonyl chloride (Eastman, used as received) with pyridine in ether: crude yield 35% as an oil; distilled yield 24%; bp 122–127° (10 Torr); nmr (CCl_4) δ 1.3 (t, 3 H, CH_3 of ethyl), 2.0 (s, 3 H, CH_3C=N), 3.0 (s, 3 H, CH_3SO_2), 4.1 (q, 2 H, CH_2 of ethyl).

E. Ethyl *N*-Benzoylacetimidate (6, R = C_6H_5).—Benzoylation of **5** gave a 74% yield from petroleum ether (bp 30–60°) of product, mp 72–74° (lit. mp 77–79°,[5] 74–75°[14]).

Synthesis of *O*-Acylhydroxylamines and Their Hydrochlorides (1 and 1·HCl).

A. *O*-Benzoylhydroxylamine hydrochloride (1·HCl, R = C_6H_5) was synthesized *via* the Carpino route[6] [**4** (R = C_6H_5) + HCl in CH_3NO_2], yield 78%, mp 117–118° dec (lit.[6] mp 120–122° dec).

B. *O*-Mesitoylhydroxylamine hydrochloride [1·HCl, R = 2,4,6-$(CH_3)_3C_6H_2$] was synthesized *via* Carpino's method[3] from **4** [R = 2,4,6-$(CH_3)_3C_6H_2$], yield 83%, mp 123° dec (lit.[3] mp 125–127° dec).

C. *O*-Mesitoylhydroxylamine [1, R = 2,4,6-$(CH_3)_3C_6H_2$] was obtained as crude oil (78% yield) from extraction with methylene chloride of 1·HCl in aqueous sodium bicarbonate.

D. *O*-Pivaloylhydroxylamine Hydrochloride (1·HCl, R = *tert*-Butyl).—Treatment of **6** (R = *tert*-butyl) with HCl and 1 equiv of water in ether gave the product as a fluocculent precipitate in 75% yield, mp 122–123° subl and dec), iodine equivalent 81.9 (calcd 76.8). The material was sublimed twice at atmospheric pressure by sealing the material into a covered petri dish and then heating the dish at 35° overnight. The resulting product, adhering to the inside lid as bulky fibers, gave an iodine equivalent of 81.8 (calcd 76.8), mp 118–121° dec. *Anal.* (of twice-sublimed material). Calcd for $C_5H_{11}NO_2$·HCl: C, 39.10; H, 7.87; N, 9.12; Cl, 23.08. Found: C, 39.21; H, 8.09; N, 8.81; Cl, 21.67.

An 80% yield of product also was obtained by treatment of **4** (R = *t*-butyl) with anhydrous HCl in ether.

E. *O*-Pivaloylhydroxylamine (1, R = *tert*-Butyl).—A chilled aqueous solution of *O*-pivaloylhydroxylamine hydrochloride was treated immediately with sodium bicarbonate until effervescence ceased. The contents then were extracted immediately with methylene chloride and the resulting organic phase was separated and dried with anhydrous sodium sulfate. Evaporation of the filtered solution under slight vacuum at room temperature left a slightly brown oil that tested positive for *O*-acylhydroxylamine (starch–iodine test) and negative for the isomeric hydroxamic acid ($FeCl_3$ complexing test), crude yield 98%.

The crude oil was distilled through a short column, bp 27° (1.2 Torr), to yield a colorless oil, $n^{28}D$ 1.4205, overall yield from the hydrochloride 87%, iodine equivalent 67.8 (calcd 58.6).

F. *O*-(4-Nitrobenzoyl)hydroxylamine hydrochloride (1·HCl, R = 4-$NO_2C_6H_4$) was synthesized by treating **4** (R = 4-$NC_2C_6H_4$) with anhydrous HCl in nitromethane, crude yield 90%, mp 218° dec.

G. *O*-(4-Nitrobenzoyl)hydroxylamine (1, R = 4-$NO_2C_6H_4$).—Treatment of the hydrochloride as in C gave a solid: mp 111.5°, 110° from methylene chloride; starch–iodide test (+); $FeCl_3$ test (−).

H. *O*-(3-Chlorobenzoyl)hydroxylamine Hydrochloride (1·HCl, R = 3-ClC_6H_4).—Treatment of **4** (R = 3-ClC_6H_4) with anhydrous HCl in nitromethane gave a fluffy solid product, mp 112–113° dec, starch–iodide test (+), $FeCl_3$ test (−).

I. *O*-(3-Chlorobenzoyl)hydroxylamine (1, R = 3-ClC_6H_4).—Treatment of the hydrochloride with aqueous sodium bicarbonate followed by extraction as in C gave the free base, mp 51–52° dec, starch–iodide test (+), $FeCl_3$ test (−).

Treatment of Hydroxylamine with Pivaloyl Chloride.—To an ice-cold suspension of pivaloyl chloride (3.88 g, 0.0321 mol) in aqueous hydroxylamine hydrochloride (2.23 g, 0.0321 mol in 6 ml of H_2O) was added a sodium bicarbonate (5.39 g, 0.0642 mol) suspension in water (10 ml). CO_2 evolved during vigorous stirring. A large amount of bulky precipitate formed immediately. Filtration and, later, chloroform extraction gave 1.74 g (46%) of crude pivalohydroxamic acid, mp 140–150° (recrystallized mp 163–164°), $FeCl_3$ test (+), starch–iodide test (−). Extraction of the aqueous filtrate with chloroform gave a negligible amount of *O*-acylhydroxylamine, along with the hydroxamic acid. Iodimetric analysis of the aqueous phase showed that 33% of the hydroxylamine remained unreacted.

Cyclohexanone Oxime.—Cyclohexanone oxime was synthesized from cyclohexanone and hydroxylamine hydrochloride in aqueous sodium acetate according to an established procedure,[15] yield 62%, mp 88–89° (lit.[15] mp 90°).

***O*-Pivaloylcyclohexanone Oxime. A.**—To a solution of pyridine (1.80 ml, 0.0224 mol) and cyclohexanone oxime (mp 88–89°, 2.54 g, 0.0224 mol) in ether (10 ml) was added pivaloyl chloride (2.70 g, 0.224 mol). The ether solution, after filtration from pyridinium chloride, removal of volatiles, and recrystallization from Cellosolve B, gave the crystalline product, 3.73 g, 84% yield, mp 54–56°, off-white in color. Snow white material was obtained by dissolving the product in methylene chloride, treating the solution with Norit A, evaporating the filtered solvent, and recrystallizing from Cellosolve B once again, yield 3.00 g (68%), mp 55.5–56.5°. *Anal.* Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.89; H, 9.88; N, 7.03.

B.—Pyridine (65 μl, 0.810 mmol) was added to a suspension of *O*-pivaloylhydroxylamine hydrochloride (124 mg, 0.810 mmol) in ether (10 ml). The formation of a new precipitate, pyridinium chloride, was apparent. To the mixture was added cyclohexanone

(11) H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

(12) W. H. Miller, A. M. Dessert, and G. W. Anerson, *J. Amer. Chem. Soc.*, **70**, 502 (1948).

(13) J. Houben and E. Schmidt, *Ber. Deut. Chem. Gesell.*, **46**, 3616 (1913).

(14) R. M. Khomutov, *J. Gen. Chem. USSR*, **31**, 1863 (1961).

(15) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 343.

(80 μl, 0.810 mmol). The contents were allowed to stand at room temperature overnight, after which they were washed with water, and the ether layer was dried with anhydrous sodium sulfate, filtered, and evaporated. This left an oily, white solid residue, mp 49–54°, yield 0.09 g (56%). Recrystallization from Cellosolve B gave white crystals, yield (0.01 g (6%), mp 54–55°, mmp 55–56° with material from procedure A. Infrared spectra of both products A and B were identical, as were tlc retention times (benzene, on silica gel).

Reaction of Triphenylphosphine with *O*-Pivaloylhydroxylamine.—A chilled solution of triphenylphosphine (K & K, 0.104 g, 0.397 mmol) in carbon tetrachloride (0.801 g) was prepared. Neat *O*-pivaloylhydroxylamine (0.0299 g, 0.255 mmol) was added, and the resulting solution was allowed to warm to room temperature while being stirred. A white precipitate of triphenylphosphine oxide quickly developed, yield 0.0555 g (78%), mp 156–157° (lit.[16] mp 156°).

Reaction of Triphenylphosphine with *O*-Pivaloylhydroxylamine Hydrochloride.—A solution of *O*-pivaloylhydroxylamine hydrochloride (0.60 g, 3.90 mmol) in absolute methanol (6 ml) was combined with a solution of triphenylphosphine (1.02 g, 3.90 mmol) in absolute methanol (10 ml). Crude iminotriphenylphosphorane hydrochloride was precipitated out of solution upon the addition of ether, yield 0.58 g (48%), mp 218° (lit.[17] mp 230–232°). *Anal.* Calcd for $C_{18}H_{17}ClNP$: Cl, 11.32. Found: Cl, 11.21. A small amount was recrystallized from methanol–ether, mp 233°. *Anal.* Calcd for $C_{18}H_{17}ClNP$: C, 68.90; H, 5.42; Cl, 11.32; N, 4.46; P, 9.89. Found: C, 69.00; H, 5.59; Cl, 11.09; N, 4.43; P, 10.10. Treatment of an aqueous solution of this product with aqueous sodium hydroxide liberates ammonia and triphenylphosphine oxide. Treatment with aqueous silver nitrate produces a white precipitate insoluble in nitric acid.

Conversion of Dibenzylamine to *N*,*N*-Dibenzylhydrazine. A.—The neat base, *O*-pivaloylhydroxylamine (0.488 g, 4.17 mmol), was added to neat dibenzylamine (Chem. Service, Media, Pa., used as received) (0.801 ml, 4.17 mmol). A slight exotherm was detectable. The contents were heated for 1 min at 100°. The $FeCl_3$ complexing test on the crude product mixture confirmed the absence of pivalohydroxamic acid. To the filtrate was added acetic acid (3 ml) and benzaldehyde (2 ml). After work-up per Carpino,[3] the dibenzylhydrazone of benzaldehyde was isolated, yield 0.18 g (14%), mp 76–78°.

B.—A solution of *O*-pivaloylhydroxylamine in chloroform-*d* was treated with dibenzylamine. The contents were sealed into an nmr tube previously flushed with nitrogen. Immediate nmr analysis showed only starting materials, in a molar ratio (amine: *O*-acylhydroxylamine) of 5:1: δ 1.2 [s, 9 H, $(CH_3)_3C$], 3.73 [s, 20 H, benzylic $(CH_2)_2$ of amine], 7.15 (m, aromatic H of amine). The sealed tube was heated for 16 hr at 78°, after which the following nmr spectrum was observed: δ 1.2 [s, 9 H, $(CH_3)_3C$], 3.67 [s, 4 H, benzylic $(CH_2)_2$ of hydrazine], 3.75 [s, 16 H, benzylic $(CH_2)_2$ of amine], 4.95 (s, NH), 7.15, (m, aromatic H). The contents were treated with benzaldehyde, per Carpino,[3] and the resulting dibenzylhydrazone of benzaldehyde was observed by thin layer chromatography. Prior to the benzaldehyde addition, the product mixture tested negative to *O*-acylhydroxylamine (starch–iodide) and negative to hydroxamic acid ($FeCl_3$).

Registry No.—**1** (R = *t*-Bu), 35657-34-2; **1** (R = *t*-Bu) HCl, 35657-35-3; **1** (R = 4-$NO_2C_6H_4$), 35657-36-4; **1** (R = 4-$NO_2C_6H_4$)HCl, 35657-37-5; **1** (R = 3-Cl-C_6H_4), 35657-38-6; **1** (R = 3-ClC_6H_4) HCl, 35657-39-7; **4** (R = *t*-Bu), 35657-40-0; **4** (R = 4-$NO_2C_6H_4$), 35657-41-1; **5**, 10576-12-2; **6** (R = *t*-Bu), 35657-43-3; **6** (R = 2,5-$Cl_2C_6H_3$), 35657-44-4; **6** (R = CF_3), 35657-45-5; ethyl *N*-methanesulfonoxyacetimidate, 35657-46-6; *O*-pivaloylcylcyclohexanone oxime, 35657-47-7; triphenylphosphine, 603-35-0; iminotriphenylphosphorane hydrochloride, 21612-82-8; benzaldehyde dibenzylhydrazone, 21136-32-3.

Acknowledgments.—The authors wish to thank Professor Daniel Swern, Associate Professor David Dalton, and Assistant Professor John Williams, all of Temple University, and the National Research Council for reviewing the original proposal. Gratitude is expressed to Mr. James W. Hampson for performing the differential scanning calorimetry experiments, and to Mrs. L. H. Scroggins and Mrs. A. S. Kravitz for elemental analyses.

(16) A. Michaelis and F. Wegner, *Chem. Ber.*, **48**, 316 (1915).
(17) H. H. Sisler, A. Arkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, **81**, 2982 (1959).

Reduction of Dehydroascorbic Acid Osazone and Related Compounds

H. EL KHADEM*

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931

Z. M. EL-SHAFEI AND M. EL SEKEILI

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

Received May 10, 1972

Reduction of dehydro-L-ascorbic acid phenylosazone (**1**) with $LiAlH_4$ resulted in the hydrogenation of the hydrazone residues and cyclization to a bicyclic compound **2**, which was dehydrated during acetylation with boiling Ac_2O to give diacetate **3**, and then partially hydrolyzed to monoacetate **4**. Reduction of the L-threo and D-erythro derivatives of 1-phenyl-3-trihydroxypropyl-4,5-pyrazoledione-4-phenylhydrazone (**5**) with Zn in AcOH afforded the bis(L-*threo*- and -(D-*erythro*-trihydroxypropyl)rubiazonic acid analogs **6**, which could be converted to the starting pyrazoles by treatment with phenylhydrazine, or oxidized with periodate to the formylrubiazonic acid.

Although the properties of reducing sugar osazones have been extensively studied,[1] the seemingly different reactions of dehydroascorbic acid osazones have only recently been investigated.[2-8] The presence of an additional carbonyl group enables dehydroascorbic acid osazones to undergo numerous cyclization reactions which do not occur with reducing sugar osazones, for example, the formation of 1-aryl-3-hydroxyalkyl-4,5-pyrazoledione-4-phenylhydrazones of type **5** by participation of the C-3 hydrazone nitrogen. This reaction is so facile that pyrazoles of this type are formed

(1) For a review, see H. El Khadem, *Advan. Carbohyd. Chem.*, **20**, 139 (1965).
(2) R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds, and F. Smith, *J. Chem. Soc.*, 1270 (1933).
(3) H. Ohle, *Ber.*, **67**, 1750 (1934).
(4) I. Antener, *Helv. Chim. Acta*, **20**, 792 (1937).
(5) H. El Khadem and S. H. El Ashry, *J. Chem. Soc.*, 2247, 2249 (1958).
(6) H. El Khadem and S. H. El Ashry, *Carbohyd. Res.*, **13**, 57 (1970).
(7) H. El Khadem, I. El Kholy, Z. M. El Shafei, and M. El Sekeili, *ibid.*, **15**, 178 (1970).
(8) H. El Khadem, M. H. Meshreki, S. H. El Ashry, and M. A. El Sekeili, *ibid.*, **21**, 430 (1972).