5.4 (t, 1 H) (J = 7 Hz); ir (liquid film) 3300 (s), 2950 (s), 1690–1700 (w), 1450 (m), 1360 (m), 1100 (s), 1000 (s), 780 (w), 675 cm^{-1} (w).

3-Methylcrotonaldehyde (8).—Dry active MnO_2 (20 g) was prepared and activated in 200 ml of distilled benzene as reported by Goldman.[7] The alcohol **7** (2.0 g) was dissolved in 5 ml of benzene and added under N_2 with stirring to the activated MnO_2. The reaction was stirred at room temperature overnight. The suspension was filtered through Celite on a Büchner funnel and washed with ethyl ether, and the filtrate was evaporated to 1.0 g of a yellow oil showing nearly pure aldehyde by nmr, yield 50%: nmr δ 2.1 (d, 6 H) (J = 11.5 Hz), 5.9 (d, 1 H) (J = 8 Hz), 10.1 (d, 1 H) (J = 8 Hz); ir (liquid film) 2750 (m), 1680 (s), 1450 (m), 1360 (m), 1200 (m), 1120 (m), 1050 (m), 830 (m), 680 cm^{-1} (m). A semicarbazone derivative melted at 221–223° (lit.[6c] mp 221–222°).

Polarography of 3-Methylcrotonaldehyde (8).—The polarographic measurements were made on a L & N, Model 62200, Type E, recording polarograph using a standard dme and sce in a 10-ml polarographic cell. The solutions were purged with N_2 for 15–20 min prior to each run. The polarographic solutions, which were 4×10^{-4} M in aldehyde, were prepared by diluting to 25 ml, 2 ml of a 0.005 M stock solution of the aldehyde with the desired 0.25 M buffer solution, resulting in pH 4.00, $E_{1/2} = -1.19$ V; pH 5.00, $E_{1/2} = -1.27$ V; pH 6.00, $E_{1/2} = -1.32$ V; pH 7.00, $E_{1/2} = -1.48$ V; pH 8.00, $E_{1/2} = -1.49$ V. The wave height was approximately 0.8 μamp at all pH values.

Controlled Potential Electrolysis of 3-Methylcrotonaldehyde (8).—The electrolysis was carried out with a Lingane-Jones[8] potentiostat in the electrolysis cell previously described. About 150 ml of pH 5.00, 0.25 M acetate buffer was placed in the cell over the pool of instrument grade mercury and purged with N_2 for 20 min. The cell was connected to the potentiostat and an initial background current was measured of 2 mA with an applied voltage of about 4 V and a reference to working electrode potential of -1.30 V. 3-Methylcrotonaldehyde (**8**), 0.50 g, in 10 cc of EtOH was then added dropwise at a rate such that the current limitations of the instrument were not exceeded (about 10 A). The electrolysis was complete within 2 hr as indicated by the return of the current to near the initial background value. The aqueous solution was extracted three times with ethyl ether, washed with saturated NaCl, and dried over Na_2SO_4. Evaporation of the solvent gave 0.53 g of a clear yellow oil, having a slight odor of acetic acid. Tlc analysis of this crude oil showed at least two mobile components when eluted with 50% ether–hexane (Eastman silica gel chromatograms). The entirec rude was chromatographed on 12 g of Silicar cc-7, eluting successively with hexane, benzene–hexane, benzene, ether–benzene, ether, ethanol, methylene chloride. Three major peaks were discernible, totaling 211 mg, 42%. The first peak, 18 mg, was eluted in 15% ether–benzene and was tentatively identified as the dihydrofuran derivative **11**. The second peak, 141 mg, eluted in 20% ether–benzene was identified as the hydroxytetrahydrofuran derivative **9**. The last significant peak, 52 mg, was eluted in 40% ether–benzene and was identified as the desired glycol (**10**). The evidence for these compounds is given below.

Component 1 (18 mg), 4,4-dimethyl-5-(2-methyl-1-propenyl)-dihydrofuran (11) (tentative): nmr δ 1.2 (d, 6 H) (J = 8 Hz), 1.7 (d, 6 H) (J = 4 Hz), 4.2 (d, 1 H), (J = 8 Hz), 5.15 (broad s, 1 H); ir 2900 (s), 1720 (w), 1690 (w), 1450 (m), 1370 (m), 1200–1050 (m), 1000 (s), 910 cm^{-1} (m).

Since **11** would obviously derive from the hydroxytetrahydrofuran derivative (**9**) by elimination of H_2O, an attempt at producing **11** from **9** by acid catalysis was made. Twenty milligrams of **9** (sublimed) was dissolved in 10 ml of dry benzene, a tiny crystal of p-toluenesulfonic acid was added, and the mixture was stirred at 45° for 12 hr under N_2. The benzene solution was then washed with H_2O, dried and evaporated, leaving a small amount of oil having a very sweet odor. Ir showed the loss of hydroxyl, and the presence of a double bond and carbonyl group. The nmr was weak and complex. The product may have been a mixture of **11** and a new aldehyde, produced by acid-catalyzed opening of the dihydrofuran system.

Component 2 (141 mg), 4,4-dimethyl-1-hydroxy-5-(2-methyl-1-propenyl)tetrahydrofuran (9): nmr δ 0.95 (d, 6 H) (J = 7 Hz), 1.75 (d, 6 H) (J = 4 Hz), 3.4 (s, 1 H), 4.4 (d, 0.25 H) (J = 9 Hz), 4.7 (d, 0.75 H) (J = 9 Hz), 5.15 (d, 1 H) (J = 9 Hz), 5.55 (t, 1 H) (J = 6 Hz); ir 3300 (w–m), 2900 (s), 1690 (w), 1450 (m), 1370 (m), 1140 (m), 1050 (m), 1005 (s), 950 (m), 910 cm^{-1} (m); mass spectrum, molecular ion at 170, intense peak at 85; precise mass 170.1313, corresponding to $C_{10}H_{18}O_2$.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.69; H, 10.62.

Component 3 (52 mg), 2,7-dimethyl-2,6-octadiene-4,5-diol (10): nmr δ 1.7 (s, 12 H), 4.15 (doublet of doublets) and 4.3 (doublet of doublets) both totaling 2 protons, (J_1 = 7 Hz, J_2 = 2 Hz for both), 5.1 and 5.25 (d, broad, 2 H total) (J = 7 Hz); ir 3500 (s), 3400 (s), 1660 (m), 1450 (s), 1380 (s), 1320 (m), 1230 (s), 1110 (s), 1040 (s), 1000 (s), 900 (w), 850 (m), 820 (m); mass spectrum, intense peak at 85 amu, no molecular ion.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.50; H, 10.56.

Registry No.—**7**, 556-82-1; **8**, 107-86-8; **9**, 28405-68-7; **10**, 28405-69-8.

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Condensation of Phenylhydroxylamine with Hydroxymethylenedesoxybenzoin

D. J. WOODMAN,* N. TONTAPANISH, AND J. V. VAN ORNUM

Department of Chemistry, University of Washington, Seattle, Washington 98105

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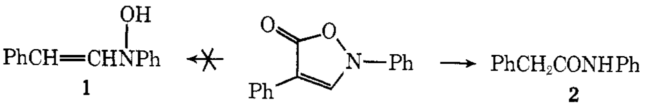
The reaction of phenylhydroxylamine with hydroxymethylenedesoxybenzoin has been shown to give derivatives of benzoylphenylacetanilide rather than the previously reported vinylhydroxylamines.

The recent finding that the postulated N-phenyl-N-styrylhydroxylamine (**1**) from the reaction of a 3-isoxazolin-5-one with aqueous base[1] is actually phenylacetanilide (**2**)[2,3] led us to reexamine the structure of other reported[4] vinylhydroxylamines from the condensation of phenylhydroxylamine with hydroxymethylenedesoxybenzoin. The reported[4] series of transformations summarized in Scheme I was of interest since the hydrolysis of the compound assigned the structure of the trans isomer of **3** had been cited in support of the incorrect structure **1**. When the hydrolysis product had been shown instead to be **2**, DeSarlo and Renzi proposed[2] that the precursor was benzoylphenylacetanilide (**5**) rather than **3** and suggested that a rearrangement might be responsible for the formation of **5**.



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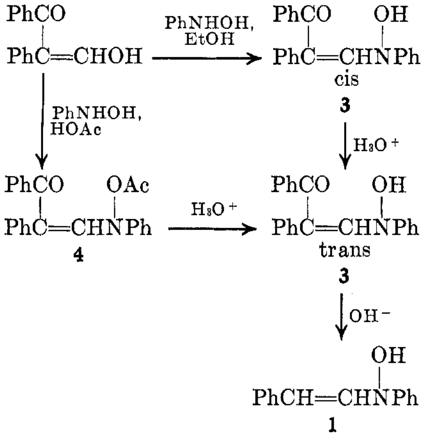
[1] H. Rupe and J. Grünholz, *Helv. Chim. Acta*, **6**, 102 (1923).

[2] F. DeSarlo and G. Renzi, *Tetrahedron*, **22**, 2995 (1966).

[3] D. J. Woodman, C. H. Borman, N. Tontapanish, and P. M. Stonebraker, *J. Org. Chem.*, **34**, 2981 (1969).

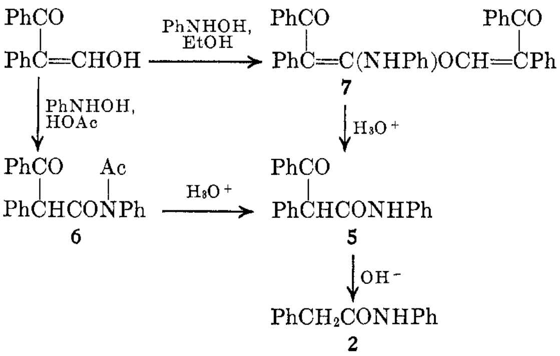
[4] H. Rupe and W. Wittwer, *Helv. Chim. Acta*, **5**, 205 (1922).

SCHEME I



Our investigation has confirmed that the compound previously thought to be the "trans" vinylhydroxylamine **3** is in fact benzoylphenylacetanilide (**5**). In addition the earlier structural assignments of **4** and the "cis" isomer of **3** also have been found to be incorrect. The actual structures are **6** and **7**, respectively, as shown in Scheme II.

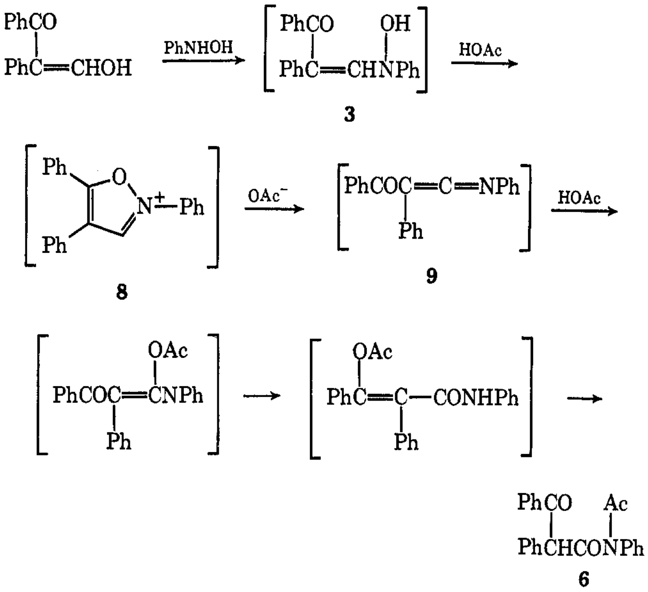
SCHEME II



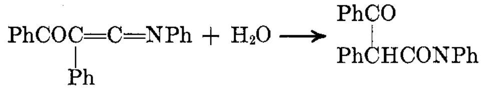
The addition of phenylhydroxylamine to a solution of hydroxymethylenedesoxybenzoin in glacial acetic acid afforded in low yield crystals having the same properties and elemental analysis as reported[4] by the earlier workers. However, the absence of long wavelength absorption in the ultraviolet spectrum indicated the compound lacked the conjugated chromophore of the proposed structure **4**. The spectral characteristics were in accord with the alternative structure of an *N*-acetyl derivative (**6**) of benzoylacetanilide.

A likely pathway to the diacylamide **6** is given in Scheme III. Although an initial condensation presumably gives the vinylhydroxylamine **3**, it apparently cyclizes to the isoxazolium cation **8** in acetic acid solution. Vinylogous hydroxamic acids closely related to the structure **3** are known to undergo this type of cyclization in the presence of acid.[5,6] The possibility of a facile cyclization with this system under conditions of moderate acidity was confirmed by the isolation of the perchlorate salt of the cation **8** from a mixture of hydroxymethylenedesoxybenzoin, phenylhydroxylamine, and perchloric acid in ether. The cyclization of **3** in acetic acid would produce an equivalent of acetate ion, and the reaction of 3-unsubstituted cations such as **8** with carboxylate ions to give diacylamides by the sequence of transformations in Scheme III is well established.[7,8] In confirmation of the structural assignment of the diacylamide **6**, an authentic sample, prepared *via* this route by treatment of the isoxazolium (**8**) perchlorate with triethylammonium acetate, was found to be identical with the material from the condensation reaction in acetic acid.

SCHEME III

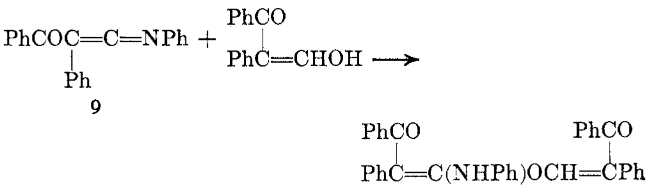


Similarly, duplication of the procedures reported[4] to give the "trans" isomer of the vinylhydroxylamine **3** gave instead a compound with the spectral properties expected for benzoylphenylacetanilide (**5**). The identity of **5** also was confirmed by comparison with an authentic sample, prepared by the hydration of the acylketenimine **9**.



$$\underset{\textstyle\mathbf{9}}{\mathrm{PhCO}\underset{\mathrm{Ph}}{\underset{|}{\mathrm{C}}}\mathrm{{=}C{=}NPh}} + \mathrm{H_2O} \longrightarrow \underset{\textstyle\mathbf{5}}{\mathrm{Ph}\overset{\mathrm{PhCO}}{\overset{|}{\mathrm{C}}}\mathrm{HCONPh}}$$

Finally, in our hands the condensation in ethanol gave a small amount of solid which underwent the reactions reported[4] for the postulated cis isomer of **3**, but the elemental composition of the material differed from that found by the previous workers. Our analyses indicated the combination of phenylhydroxylamine with two equivalents of the carbonyl compound. In this case again it appears that cyclization to **8** and ring opening have taken place, since we obtained the identical compound by addition of hydroxymethylenedesoxybenzoin to the acylketenimine **9**. While the spec-



$$\underset{\textstyle\mathbf{9}}{\mathrm{PhCO}\underset{\mathrm{Ph}}{\underset{|}{\mathrm{C}}}\mathrm{{=}C{=}NPh}} + \mathrm{Ph}\overset{\mathrm{PhCO}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CHOH} \longrightarrow \underset{\textstyle\mathbf{7}}{\mathrm{Ph}\overset{\mathrm{PhCO}}{\overset{|}{\mathrm{C}}}\mathrm{{=}C(NHPh)OCH{=}}\overset{\mathrm{PhCO}}{\overset{|}{\mathrm{C}}}\mathrm{Ph}}$$

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[5] R. B. Woodward and D. J. Woodman, *J. Org. Chem.*, **31**, 2039 (1966).

[6] D. J. Woodman and Z. L. Murphy, *ibid.*, **34**, 1468 (1969).

[7] R. B. Woodward and R. A. Olofson, *J. Amer. Chem. Soc.*, **83**, 1007 (1961); *Tetrahedron Suppl.*, **7**, 415 (1966).

[8] R. B. Woodward, D. J. Woodman, and Y. Kobayashi, *J. Org. Chem.*, **32**, 388 (1967).

tral properties are in agreement with the simple adduct **7**, the possibility of migrations of the PhCOC(Ph)=CH— group to give some other derivative of **5** from **7** cannot be excluded on the basis of our data.

Experimental Section

2,4,5-Triphenylisoxazolium Perchlorate (8).—A mixture of 2.41 g (10.8 mmol) of hydroxymethylenedesoxybenzoin and 1.21 g (11.1 mmol) of *N*-phenylhydroxylamine in 75 ml of dry ether was stirred vigorously with protection from light while 1.5 ml of 70% $HClO_4$ was added dropwise. Stirring was continued several hours, and the solution was stored overnight in a refrigerator. The next day a dark precipitate was removed by filtration, washed with ether, and dried. Precipitation of the crude product from acetone with ether gave 2.52 g (59%) of solid: mp 137–138° dec; uv $\lambda_{\max}^{0.1\,M\,\mathrm{HCl}}$ 250 mμ (ϵ 15,700) and 333 (3000); nmr (MeCN) τ 0.26 and aromatic signals centered at τ 2.4.

Anal. Calcd for $C_{21}H_{16}ClNO_5$: C, 63.36; H, 4.03; Cl, 8.94; N, 3.52; O, 20.14. Found: C, 63.24; H, 4.13; Cl, 8.81; N, 3.65; O, 20.19.

Benzoylphenylacetanilide (5).—A suspension of 0.201 g (0.5 mmol) of the perchlorate of **8** in water containing excess (0.2 ml) triethylamine was stirred 2 hr with warming in a hot-water bath, giving a yellow solid which was removed by filtration. One recrystallization from acetic acid followed by two recrystallizations from ethanol-water gave 0.117 g (73.5%) of **5**: mp 170–171° (lit.[4] 166°); ir (KBr) 3.07 (NH), 5.98 (C=O), 6.02 (amide I), 6.47 (amide II) μ; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 228 mμ; nmr τ 4.33 (s, 1.0), 2.57 (s, 10.0), and 0.70 (br, 0.99).

Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44; O, 10.15. Found: C, 79.84; H, 5.49; N, 4.56; O, 10.11.

***N*-Acetylbenzoylphenylacetanilide (6). Preparation from Hydroxymethylenedesoxybenzoin.**—To a solution of 0.224 g (1.00 mmol) of hydroxymethylenedesoxybenzoin in 0.2 ml of glacial acetic acid was added in portions 0.122 g (1.12 mmol) of phenylhydroxylamine. The brown solution was stirred for 2–3 hr, warmed briefly, and partitioned between CH_2Cl_2 and water. The organic phase was dried (Na_2SO_4) and evaporated. Recrystallization of the residue first from ethanol and then from benzene gave 0.082 g (23%) of **6**: mp 158–160° (lit.[4] 157–158°); ir (KBr) 5.86, 5.99, and 6.27 μ; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 245 mμ (ϵ 15,800); nmr τ 7.93 (s, 3.04), 3.45 (s, 0.97), and 2.72 (s, 10.00).

Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.28; H, 5.36; N, 3.92; O, 13.44. Found: C, 77.21; H, 5.48; N, 4.07; O, 13.24.

Preparation from the Perchlorate of 8.—Excess (0.15 ml) Et_3N was added dropwise to a suspension of 0.203 g (0.51 mmol) of the perchlorate of **8** in cold CH_2Cl_2. Immediately excess (0.2 ml) HOAc was added dropwise to the stirred solution over a period of 15 min and the solution was stirred for 4 hr. The solution was diluted with an equal volume of benzene, partially evaporated to precipitate the bulk of the triethylammonium salts, and partitioned between CH_2Cl_2 and water. The organic phase was dried (Na_2SO_4) and evaporated. Recrystallization of the residue from ethanol gave 0.120 g (66%) of **6**, having melting point and mixture melting point identical with that of **6** above.

Hydrolysis of 6 to 5.—A mixture of 0.127 g (0.36 mmol) of **6**, and 10 drops of concentrated H_2SO_4 in 10 ml of EtOH was heated under reflux overnight. A solid precipitated upon dilution with an equal volume of water. Recrystallization from EtOH–water gave 0.042 g (37%) of **5**, having melting point and mixture melting point identical with that of **5** above.

Condensation of Phenylhydroxylamine and Hydroxymethylenedesoxybenzoin.—Phenylhydroxylamine, 0.091 g (0.84 mmol), was added in portions over a period of 14 min to a suspension of 0.177 g (0.79 mmol) of hydroxymethylenedesoxybenzoin in 3 ml of absolute EtOH in a dry reaction vessel. Stirring the mixture for 5-6 hr produced a milky yellow solution. Evaporation of the solvent and recrystallization of the residue from benzene gave 0.068 g (17%) of solid: mp 164–166°;[9] ir (KBr) 3.06 (NH), 6.08, 6.20, and 6.52 μ; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 354 mμ (ϵ 13,600); nmr τ 2.93 (25) and −0.32 (s, 1).

Anal. Calcd for $C_{36}H_{27}NO_3$: C, 82.89; H, 5.22; N, 2.69; O, 9.20. Found: C, 83.12, 83.08; H, 5.36; 5.30; N, 2.68, 2.66; O, 9.07, 9.08.

Reaction of Hydroxymethylenedesoxybenzoin, Triethylamine, and the Perchlorate of 8.—To a solution of 0.402 g (1.01 mmol) of the perchlorate of **8** in CH_2Cl_2 was added dropwise an excess (0.25 ml) of triethylamine. A dark reddish brown solution was obtained after stirring for 3–4 hr. Triethylammonium perchlorate was precipitated by repeated dilution with an equal volume of benzene, partial evaporation, and decantation. Hydroxymethylenedesoxybenzoin, 0.228 g (1.02 mmol), was added to the cold benzene solution, and the mixture was allowed to stand overnight in a refrigerator. Filtration, washing the solid with benzene, and air-drying gave 0.295 g (56%) of material having melting point and mixture melting point identical with that of the above product.

Registry No.—**5**, 22468-40-2 **6**, 28478-23-1; **8**, 28537-45-3; phenylhydroxylamine, 100-65-2; hydroxymethylenedesoxybenzoin, 28478-24-2.

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(9) The reported[4] melting point (158°) was obtained for the crude product. The compound underwent thermal decomposition to an uncharacterized compound of the same melting point and elemental analysis as reported by the previous workers.