Fraction B. Boiling point 16–20°, 85 g., mol. wt. 219–228; reported[4] for SF_5CF_2COF, b.p. 22°, mol. wt. 224. Since a gas chromatograph showed four to six components over this boiling range a 2 g. sample was quantitatively chromatographed, using a stationary phase of the ethyl ester of Kel-F acid 8114, on Celite. About 75% of this amount, representing approximately 63 g. of the whole fraction, was recovered as one peak, mol. wt. 250, and was identified as $(CF_3)_2SF_4$ by comparison of its infrared spectrum with that of known $(CF_3)_2SF_4$, b.p. 20°, mol. wt. 246. The remainder of the chromatographed material had an average mol. wt. of only 148.

Fraction C. Boiling point 47.5°, 24 g., mol. wt. 297, purity 99%. An infrared spectrum showed all peaks found in the spectrum of $CF_3SF_4CF_2CF_3$, b.p. 47.1°, mol. wt. 296, but also additional lines at 10.80–10.85 and 12.25, and an elemental analysis was therefore made.

Anal. Calcd. for $C_3F_{12}S$: C, 12.2; F, 77.1; S, 10.8. Found: C, 12.4; F, 76.8; S, 11.0.

Fraction D. Boiling point 55°, 39 g., mol. wt. 279 (calcd. for $CF_2SF_4CF_2COF$ 274), purity 83%. An infrared spectrum showed a sharp peak for −COF at 5.27. Because of the impurities present, this compound was converted for analysis to the methyl ester (67% yield) by refluxing with methanol. The ester had b.p. 123°, n_D^{30} 1.3259.

Anal. Calcd. for $C_4H_9H_3O_2$: C, 16.8; F, 59.7; H, 1.1; S, 11.2. Found: C, 17.1; F, 59.0; H, 1.1; S, 10.9.

Principal infrared lines for these two new compounds are: $CF_3SF_4CF_2COF$ 5.27, 7.80, 7.90–7.95, 8.06, 9.70, 10.12 (w), 10.83, 11.32 (w), 11.65–11.80, 12.50, 14.00–14.05, 14.85–14.95; $CF_3SF_4CF_2COOCH_3$ (in CCl_4) 5.60, 6.95, 7.62, 8.00–8.05, 8.17, 8.63–8.73, 9.95, 11.90–12.00, 12.18, 14.50.

Fraction E. Boiling point 87–88°, 10 g., mol. wt. 352, n_D^{28} 1.2964, purity 95%. Refluxing with 30% aqueous KOH did not change the mol. wt. and no sign of reaction was observed. Identified by NMR, as discussed above. Principle infrared lines for this compound are 7.95, 8.63, 10.85–11.05, 11.65–11.75, 12.75, 14.25–14.50.

Anal. Calcd. for $C_2F_{14}S_2$: F, 75.2; S, 18.0; mol. wt. 354. Found: F, 75.1; S, 18.0; mol. wt. 352.

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Structure of the Reaction Product of Phenyl Vinyl Ketone and Hydroxylamine

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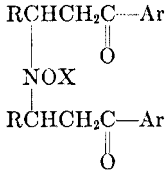
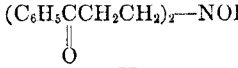
Under the proper conditions, the reaction of certain α,β-unsaturated aryl ketones (or a precursor of the unsaturated ketone) with methoxyamine, substituted hydroxylamines, or hydroxylamine has been reported to yield bisketoamines analogous to structure I.[2]



X = H or CH_3

I

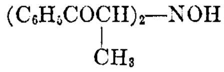
In line with this, Auwers and Müller[3] have described a compound melting at 140° to which they assigned the structure bis(β-benzoylethyl)hydroxylamine (II). This material was prepared from the



$$(C_6H_5\underset{\underset{O}{\|}}{C}CH_2CH_2)_2\text{—}NOH$$

II

corresponding dioxime, which in turn resulted from the treatment of β-chloropropiophenone with free hydroxylamine and excess alkali. Shortly before this, Danilowa and Danilow[4] had reported a compound melting at 122.5° (obtained from the reaction of a 1:1 ratio of phenyl vinyl ketone and free hydroxylamine) to which they assigned structure III. Both groups reported a compound melting at



$$(C_6H_5CO\underset{\underset{CH_3}{|}}{C}H)_2\text{—}NOH$$

III

153–154° which they described as the dioxime of the respective dicarbonyl compounds (II and III).

In the present work, the reaction of phenyl vinyl ketone with hydroxylamine hydrochloride in the presence of sodium acetate produced compounds which were demonstrated to be bis(β-benzoylethyl)-hydroxylamine (II), m.p. 120.5–121°, or the dioxime (m.p. 148–149°) of this compound. With hydroxylamine hydrochloride and sodium acetate the dicarbonyl compound could be readily converted into the dioxime, but repeated recrystallizations from three different solvents failed to raise the melting point of the dioxime (148–149°) to the value reported by Auwers[3] and Danilowa.[4] In order to clarify the structure of these compounds two similar compounds were prepared for a comparative nuclear magnetic resonance study; bis(β-benzoylethyl)methoxyamine (IV) was produced in 53% yield from phenyl vinyl ketone and methoxyamine hydrochloride and bis[β-(p-methoxybenzoyl)ethyl]-

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[2] (a) A. H. Blatt, *J. Am. Chem. Soc.*, **61**, 3494 (1939). (b) J. Thesing, A. Müller, and G. Michel, *Chem. Ber.*, **88**, 1027 (1955). (c) E. Profft, F. Runge, and A. Junar, *J. prakt. Chem.*, [4], **1**, 57 (1954).

[3] K. v. Auwers and H. Müller, *J. prakt. Chem.*, [NF], **137**, 102 (1933).

[4] E. Venus Danilowa and S. Danilow, *J. Gen. Chem. (U.S.S.R.)*, **2**, 645 (1932); *Chem. Abstr.*, **27**, 1624[5] (1933).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR SUBSTITUTED HYDROXYLAMINES

	$\Delta\nu^a$	Area[b] Ratio	Assignment	$\Delta\nu$	Area Ratio	Assignment	$\Delta\nu$	Area Ratio	Assignment	$\Delta\nu$	Area Ratio	Assignment
II	57.6	1.28 (1.25)	—CH_2—									
Acetate of II	53.5	1.24 (1.25)	—CH_2—	109.6	2.74 (2.67)	CH_3CO						
IV	57.3	1.24 (1.25)	—CH_2—				47.1	3.17 (3.33)	$NOCH_3$			
V	58.0	0.98 (1.0)	—CH_2—				46.1	2.72 (2.66)	$NOCH_3$	32.9	1.44 (1.33)	$ArOCH_3$

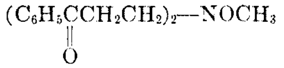
[a] Expressed in cycles/second from water at a frequency of 40 M.c.p.s. The sign convention is such that positive values of $\Delta\nu$ represent signals observed at a higher field than that of water. [b] Area ratio: aromatic peaks (at −83 to −143)/observed peak; ( ) is the theoretical values for compounds having structure.

$$(YC_6H_4COCH_2CH_2)_2\text{—}NOX$$

$$Y = H \text{ or } CH_3O$$

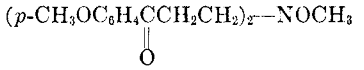
$$X = H, CH_3, \text{ or } COCH_3$$

methoxyamine (V) was produced in 28% yield from *p*-methoxyphenyl vinyl ketone and methoxyamine hydrochloride.



$(C_6H_5\overset{\|}{\underset{O}{C}}CH_2CH_2)_2\text{—}NOCH_3$

IV



$(p\text{-}CH_3OC_6H_4\underset{O}{\overset{\|}{C}}CH_2CH_2)_2\text{—}NOCH_3$

V

An examination of these compounds by nuclear magnetic resonance produced rather anomalous results. For compounds having structure I (where R = H), significantly different chemical shifts would be expected for the chemically different methylene groups. In the spectra of II, the acetate of II, IV, and V, this distinction was not observed; in all cases a single sharp peak assignable to the methylene groups was found. Comparison of the integrated area of the peaks produced by the aromatic hydrogens with the areas of peaks resulting from the other hydrogens provided strong support for the presence of a -CH_2—CH_2— grouping in these molecules. These data are summarized in Table I. The area measurements were also found to be internally consistent for a given compound. For the acetate of II, the ratio —CH_2—/CH_3CO was 2.74 (theoretical: 2.67 for 8/3). For compound IV, the ratio —CH_2—/$NOCH_3$ was 2.55 (theoretical: 2.67 for 8/3). And for compound V the area ratios were: —CH_2—/$NOCH_3$, 2.77 (theoretical: 2.67 for 8/3); —CH_2—/$ArOCH_3$, 1.47 (theoretical: 1.33 for 8/6); $ArOCH_3$/$NOCH_3$, 1.88 (theoretical: 2.0 for 6/3).

Substantial proof for two of these structural assignments was provided by the Clemmenson reduction of II to bis(γ-phenylpropyl)amine which was isolated and identified as the hydrochloride. This established the structure of II and the dioxime of II, and when considered in conjunction with the similarities in manner of synthesis, comparable infrared data, and nuclear magnetic resonance data, constituted strong support for the structural assignments offered for IV and V.

EXPERIMENTAL

Bis(β-benzoylethyl)hydroxylamine (II). To 3.77 g. (0.046 mole) of anhydrous sodium acetate dissolved in 75 ml. of water was added 2.0 g. (0.015 mole) of phenyl vinyl ketone[5] suspended in 80 ml. of water and 10 ml. of ethanol. Stirring was started and the solution was cooled to 0°; 3.12 g. (0.045 mole) of hydroxylamine hydrochloride in 75 ml. of water was then added to the vigorously stirred mixture during 10 min. After 90 min. at 0°, the precipitated white solid was collected on a filter and air dried. Crude yield: 1.92 g. (86.4%), m.p. 115–118°. Recrystallization from absolute ethanol produced fine white crystals, m.p. 120.5–121°. Significant infrared bands (chloroform): 3420–3300 (—OH); 1680 (ArC=O); 1602, 1586, 1497 (aromatic); 1455; 1374; 1325; 1282; 975; and 685 cm.$^{-1}$ Ultraviolet maxima (absolute ethanol): λ_{max} 242 mμ (ϵ 23,700), λ_{max} 280 mμ (ϵ 2,390). Nuclear magnetic resonance data have been summarized in Table I.

Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71; O, 16.14. Found: C, 72.63; H, 6.50; N, 4.78; O, 16.18. Mol. wt. calcd.: 297. Mol. wt. (ebullioscopic in butanone): 302.

Acetate of bis(β-benzoylethyl)hydroxylamine. bis(β-Benzoylethyl)hydroxylamine (0.300 g., 0.001 mole) dissolved in 14 ml. of chloroform was allowed to react with 0.122 g. (0.0012 mole) of acetic anhydride in 5 ml. of glacial acetic acid at 0°. After 0.5 hr. at 0°, the reaction was stirred at room temperature for 16 hr. The mixture was then washed with a dilute solution of sodium bicarbonate, the chloroform layer separated, dried over sodium sulfate, and evaporated to dryness. The residue was recrystallized from absolute ethanol; yield: 0.240 g. (71%); m.p. 90–91°. Significant infrared

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[5] C. S. Marvel and Donald J. Casey, *J. Org. Chem.*, in press.

bands (chloroform): 2995, 2900, 2860, 1755, 1682, 1600, 1583, 1452, 1370, 1326, 1194, 1004, 970, 917, and 687 cm.$^{-1}$ Nuclear magnetic resonance data have been listed in Table I.

Anal. Calcd. for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.80; H, 6.43; N, 4.04.

Dioxime of bis(β-benzoylethyl)hydroxylamine. Solutions of 2.0 g. (0.015 mole) of phenyl vinyl ketone in 50 ml. of ethanol and 2.38 g. (0.029 mole) of anhydrous sodium acetate in 75 ml. of ethanol were added at equivalent rates to a stirred solution of 2.09 g. (0.030 mole) of hydroxylamine hydrochloride in 50 ml. of ethanol at 0°; addition time: 15 min. The mixture was stirred at 0° for 90 min., allowed to warm to room temperature, and the inorganic salt removed by filtration. The ethanol solution was then concentrated under reduced pressure to 25 ml., and 150 ml. of water was added gradually to precipitate 2.26 g. (92%) of crude product. This material was washed thoroughly with chloroform and recrystallized from methanol to yield 1.72 g. (70%) of pure dioxime; m.p. 148–149°. Pertinent infrared bands (Nujol): 3310, 1630 (weak), 1600 (weak), 1577 (weak), 1503, 1323, 1312, 1024, 933, 810, 765, 758, and 688 cm.$^{-1}$

Anal. Calcd. for $C_{18}H_{21}N_3O_3$: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.77; H, 6.52; N, 12.75. Mol. wt. calcd.: 327. Mol. wt. (ebullioscopic in butanone): 346.

Bis(β-benzoylethyl)hydroxylamine was converted to the dioxime by treatment with slightly more than a two-fold excess of hydroxylamine hydrochloride and sodium acetate in ethanol at room temperature. The yield was 80%.

Bis(β-benzoylethyl)methoxyamine (IV). Anhydrous sodium acetate (2.38 g., 0.029 mole) in 50 ml. of ethanol and methoxyamine hydrochloride (2.42 g., 0.029 mole) in 50 ml. of ethanol were added at equivalent rates to a stirred solution of phenyl vinyl ketone (3.6 g., 0.027 mole) in 50 ml. of ethanol at 0°; addition time: 15 min. After 1 hr. at 0°, the precipitated sodium chloride was removed by filtration and the ethanol solution concentrated to 20 ml. under reduced pressure. The precipitated solid was collected on a filter, washed well with water, and recrystallized from absolute ethanol; yield: 2.24 g. (53%); m.p. 93–94. Significant infrared bands (chloroform): 3000, 2935, 2890, 1680, 1598, 1582, 1463 (shoulder), 1452, 1371, 1324, 1180, 1035, 1003, 973, and 687 cm.$^{-1}$ The spectrum was strikingly similar to that of bis(β-benzoylethyl)hydroxylamine. Nuclear magnetic resonance data have been presented in Table I.

Anal. Calcd. for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.31; H, 6.68; N, 4.71.

p-Methoxy-β-chloropropiophenone. p-Methoxy-β-chloropropiophenone was prepared by a modification of the procedure of Davies and Powell.[6] To 83 g. (0.62 mole) of anhydrous aluminum chloride was added with stirring and cooling in an ice bath a solution of 69.9 g. (0.55 mole) of β-chloropropionyl chloride in 90 ml. of carbon disulfide, followed by 67.2 g. (0.62 mole) of freshly distilled anisole in 120 ml. of carbon disulfide. The ice bath was removed and the reaction heated under reflux for 1 hr. after which the mixture was poured onto cracked ice with stirring. Chloroform was added and the layers separated. The aqueous layer was extracted with chloroform and the washings combined with the original organic phase which was then washed with water and dried over sodium sulfate. Evaporation of the solvent under reduced pressure left a solid which was recrystallized from a 70:30 mixture of medium high boiling (b.p. 60–90°) and low boiling (b.p. 30–60°) petroleum ether; yield: 88 g. (81%); m.p. 63–64° [lit., 63,[6] 63–64[7]]. Significant infrared bands (chloroform): 3000 (shoulder), 2960, 2835, 1673, 1600, 1578, 1513, 1465, 1425, 1365–1353, 1310, 1260, 1243, 1170, 1114, 1030, 982, and 835 cm.$^{-1}$.

Bis[β-(p-methoxybenzoyl)ethyl]methoxyamine (V). Solutions of *p*-methoxy-β-chloropropiophenone (5.88 g., 0.0296 mole) in 25 ml. of ethanol and potassium acetate (2.90 g., 0.0296 mole) in 25 ml. of ethanol were mixed and heated briefly. After 45 min. the precipitated potassium chloride was removed by filtration. To this ethanol solution of *p*-methoxyphenyl vinyl ketone was added at once 2.47 g. (0.0296 mole) of methoxyamine hydrochloride in 50 ml. of ethanol. Stirring was started and 2.43 g. (0.0296 mole) of sodium acetate in 50 ml. of ethanol was added over a period of 10 min.; the reaction was then stirred at room temperature for 2 hr. The precipitated sodium chloride was removed, the ethanol solution concentrated to 10 ml., and the resulting solid collected on a filter. This material was recrystallized once from medium high boiling petroleum ether (b.p. 60–90°) and then from absolute ethanol. Yield: 1.55 g. (28%); m.p. 111.5–112.6°. A 34% yield of the same product was obtained by substituting a drop of concentrated hydrochloric acid for the sodium acetate in the above procedure. Pertinent infrared bands (chloroform): 3000 (shoulder), 2930, 2830, 1671, 1598, 1575, 1510, 1464, 1445, 1421, 1369, 1313, 1260, 1240–1220, 1168, 1113, 1030, 981, and 835 cm.$^{-1}$. Nuclear magnetic resonance data have been recorded in Table I.

Anal. Calcd. for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.77. Found: C, 67.79; H, 6.81; N, 3.62.

Reduction of bis(*β-benzoylethylhydroxylamine*). Zinc dust (7.2 g., 0.11 mole), mercuric chloride (0.72 g., 0.0026 mole), 1 ml. of concentrated hydrochloric acid, and 10 ml. of water were shaken together for 5 min.; the supernatant liquid was then decanted and discarded. To the amalgamated zinc were added in order: 4.5 ml. of water, 10.5 ml. of concentrated hydrochloric acid, and 0.997 g. (0.0034 mole) of bis-(β-benzoylethyl)hydroxylamine in 15 ml. of reagent grade benzene. The mixture was then heated at reflux temperature for 24 hr. with an additional 1.5 ml. of concentrated hydrochloric acid being added every 6 hr. At the end of this period the reaction mixture was cooled and the solution decanted. The insoluble oil clinging to the walls of the reaction flask was dissolved in ethanol, the ethanol solution filtered to remove particles of zinc, and the solvent evaporated. The residual oil was treated with dilute sodium hydroxide solution, the basic solution extracted with chloroform, and the chloroform solution evaporated to dryness. The residual yellow oil was repeatedly extracted with hot dilute hydrochloric acid and the combined acid solutions evaporated to dryness leaving small white plates. After 5 recrystallizations from water, 0.155 g. (16%) of bis(γ-phenylpropyl)amine hydrochloride was obtained; m.p. 214.5–215.5° (lit., 203°[8]). An additional 0.394 g. of intractable oil was also isolated. Pertintent infrared bands (chloroform): 3400 (very weak), 3010 (shoulder), 2950, 2760, 2460, 1653 (very weak), 1600 (shoulder), 1582, 1494, 1465 (shoulder), 1453, 969, and 690 cm.$^{-1}$

Anal. Calcd. for $C_{18}H_{24}NCl$: C, 74.59; H, 8.34; N, 4.83; Cl, 12.23. Found: C, 74.63; H, 8.08; N, 4.69; Cl, 12.04. Mol. wt. calcd.: 290. Mol. wt. (Signer[9] in chloroform): 309.

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(6) R. E. Davies and G. Powell, *J. Am. Chem. Soc.*, **67**, 1466 (1945).

(7) J. Kenner and F. S. Statham, *J. Chem. Soc.*, 299 (1935).

(8) K. Kindler, *Ann.*, **431**, 187 (1923).

(9) A. Steyermark, *Quantitative Organic Microanalysis*, Blakiston, Co., Philadelphia, Pa., 1951, p. 292.