compound (3.1 g, 0.02 mole) in the presence of 0.08 mole of sodium nitrite. Evaporation of the ethyl acetate extract left 1.0 g (48%) of the crude product. It crystallized from ethanol or water as colorless needles, mp 250°. A mixture melting point with 5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra were identical.

Desulfurization of 7-Amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (16, R = H) with Hydrogen Peroxide.—A mixture of the thiol (1.6 g, 0.1 mole) and barium chloride dihydrate (2.4 g, 0.01 mole) was suspended in concentrated hydrochloric acid (12 *N*, 25 ml). The mixture was stirred and aqueous hydrogen peroxide (30%, 3.5 g, 0.03 mole) in water (10 ml) was added dropwise over a period of 10 min. After heating the solution at 80-90° for 1 hr, it was cooled and filtered to remove barium sulfate. The filtrate was neutralized and evaporated to dryness and the residue was extracted with three 50-ml portions of hot, absolute ethanol. The combined extracts were evaporated to dryness and the residue was continuously extracted with hot ethyl acetate for 48 hr. Evaporation of the extract left 0.8 g of crude 7-amino-7H-*s*-triazolo[5,1-*c*]-*s*-triazole, mp 210–220°. Two recrystallizations from ethanol gave the amino compound as colorless platelets: yield, 0.2 g (18%); mp 225°; infrared (cm^{-1}) main bands at 3236, 3048, 1597, 1529, 1243, 1223, 1193, 1126, 1025, 980, 952, 917, 840, 826, 740, 626.

Desulfurization of 5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = H; R′ = SH) (1.4 g, 0.01 mole) by the hydrogen peroxide method gave 0.6 g (58%) of 5H-*s*-triazolo[5,1-*c*]-*s*-triazole, mp 250°. A mixture melting point with a sample prepared by deamination of 3-amino-5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra of the two products were identical.

The residue, insoluble in ethyl acetate, was dissolved in water (25 ml). The resulting, slightly basic solution was neutralized and the pale yellow solid that separated was filtered off and recrystallized from a large volume of water, giving 0.2 g of product, mp 250°. A mixture melting point with 5H-*s*-triazolo[5,1-*c*]-*s*-triazol-3-yl disulfide was not depressed and the infrared absorption spectra of the two products were identical.

Repeating the reaction as above, except that no barium chloride was added, gave, as the only product, the disulfide: yield, 0.5 g (30%); mp 250°.

Desulfurization of 6-Methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = CH_3; R′ = SH).—The thiol (0.7 g, 0.005 mole) was dissolved in water (20 ml) containing sodium hydroixde (0.4 g, 0.01 mole). The solution was stirred and aqueous hydrogen peroxide (30%, 1.2 g, 0.01 mole) was added dropwise over a period of 10 min. After stirring the reaction mixture for 3 hr at room temperature, it was treated with concentrated sulfuric acid (20 ml) and diluted with water (75 ml). After standing overnight, the solution was neutralized (pH 7) and evaporated to dryness. The residue was extracted with three 50-ml portions of hot, absolute ethanol and the combined extracts were evaporated to dryness. The residue was extracted continuously with hot ethyl acetate for 24 hr and evaporation of the extract gave 0.4 g (66%) of crude 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole. Crystallization from water gave colorless, irregular prisms, mp 235°. A mixture melting point with a sample prepared by deamination of 3-amino-6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole was not depressed and the infrared absorption spectra of the two products were identical.

Desulfurization of 6-phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole-3-thiol (1, R = Ph; R′ = SH) (0.7 g, 0.004 mole) was carried out by the procedure described immediately above. 6-Phenyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole crystallized from ethanol–water as colorless needles: yield, 0.3 g (50%); mp 215°.

Registry No.—**1a**, 14661-17-7; **1b**, 14661-18-8; **1c**, 6388-02-9; **1d**, 13728-21-7; **1e**, 13728-22-8; **1f**, 3529-51-9; **1g**, 14661-23-5; **1h**, 14661-24-6; **1i**, 13728-18-2; **1j**, 13728-20-6; **1k**, 13728-23-9; **1l**, 14661-28-0; **1m**, 14661-29-1; **1n**, 13728-15-9; **1o**, 13728-26-2; **1p**, 14661-32-6; **1q**, 14661-33-7; **1r**, 13728-28-4; **1s**, 14661-35-9; **1t**, 14661-36-0; **1u**, 14661-37-1; **1v**, 13728-27-3; **1w**, 13728-29-5; **1x**, 14661-40-6; **1y**, 14661-41-7; **1z**, 251-93-4; **1aa**, 13728-25-1; **1bb**, 14661-44-0; **1cc**, 6219-30-3; **2** (R = H; R′ = NH_2), 14723-34-3; **2** (R = CH_3; R′ = NH_2), 14661-46-2; **18**, 1750-12-5; **20** (R = H), 14661-47-3; **20** (R = CH_3), 14661-59-7.

Acknowledgment.—The authors are indebted to Professor H. Gehlen for a sample of 6-methyl-5H-*s*-triazolo[5,1-*c*]-*s*-triazole.

Reactions of O-Benzoyl Oximes with Sodium Hydride. Substituted Isoxazoles and the Neber Rearrangement[1]

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4-Benzoyl-3,5-diphenylisoxazole and a derivative of phenacylamine have been isolated from the reaction products of acetophenone O-benzoyl oxime with sodium hydride. Corresponding products were obtained from *para*-substituted acetophenone O-benzoyl oximes. Propiophenone O-benzoyl oxime, cyclohexanone O-benzoyl oxime, and acetophenone O-(2,4,6-trimethylbenzoyl) oxime gave Neber rearrangement products but no isoxazoles.

The reaction between O-benzoyl oximes and sodium hydride offers interesting possibilities for condensation and elimination reactions. Acetophenone O-benzoyl oxime (**1a**) in boiling toluene reacted smoothly with sodium hydride to evolve an approximately equimolar amount of hydrogen. The reaction mixture was treated with dilute hydrochloric acid and the organic layer subsequently extracted wih sodium carbonate solution. Acid-soluble, base-soluble, and neutral products were isolated.

The acid-soluble product polymerized when the solution was made basic, but was identified as phenacylamine hydrochloride (**2**) by conversion to the N-benzoyl derivative (**3a**). The reaction leading to this product seems properly classified as a Neber rearrangement.[2] 3-Phenyl-2H-azirine (**4**) is probably an intermediate.[3]

The base-soluble product was identified as benzoic acid.

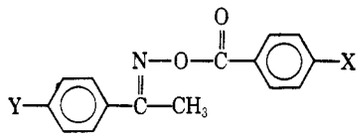
Neutral products of the reaction included acetophenone oxime and a new[4] compound shown to be 4-benzoyl-3,5-diphenylisoxazole (**5a**). The structure of **5a** was deduced from elemental analysis, molecular weight determination, strong absorption at 6.05 μ (C=O), and

(1) Supported by National Science Foundation URP Grants G-22895 and GY-215.

(2) P. W. Neber and A. Friedoesheim, *Ann.*, **449**, 109 (1926).

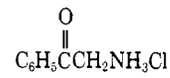
(3) C. O'Brien, *Chem. Rev.*, **64**, 81 (1964); D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *J. Org. Chem.*, **30**, 579 (1965).

(4) An isomer, 5-benzoyl-3,5-diphenylisoxazole, has been reported: E. P. Kohler, *J. Am. Chem. Soc.*, **47**, 3032 (1925).

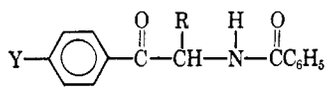


1, 5, 6a, Y = X = H
b, Y = H; X = Cl
c, Y = H; X = CH_3
d, Y = Cl; X = H
e, Y = CH_3; X = H
f, Y = X = Cl
g, Y = Cl; X = CH_3

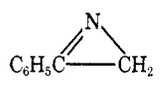
1a–g



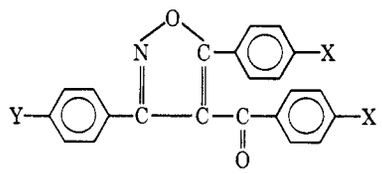
2



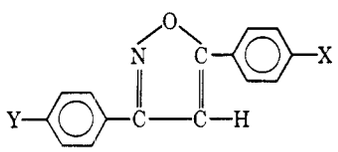
3a, R = Y = H
b, R = H; Y = Cl
c, R = H; Y = CH_3
d, R = CH_3; Y = H



4

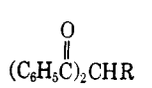


5a–g

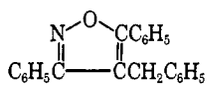


6a–g

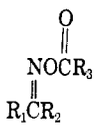
conversion to 3,5-diphenylisoxazole (**6a**) and potassium benzoate by heating with potassium hydroxide in 2,2′-oxydiethanol. Attempts to confirm the structure of **5a** by synthesis from tribenzoylmethane (**7b**) and hydroxylamine were unsuccessful. Under conditions which converted dibenzoylmethane (**7a**) to **6a**, and benzyldibenzoylmethane (**7c**) to 3,5-diphenyl-6-benzylisoxazole (**8**) in good yields tribenzoylmethane reacted only partially to form **6a**. Apparently **7b** reacts with hydroxylamine to form **7a** (subsequently converted to **6a**) and benzohydroxamic acid, but we did not look for benzohydroxamic acid among our products. The structure of **5a** was confirmed by reduction to **8** and comparison with the same compound prepared from **7c** and hydroxylamine.



7a, R = H
b, R = PhCO
c, R = $PhCH_2$



8



9a, $R_1 = R_3 = Ph$; $R_2 = Et$
b, $R_1 = Ph$; $R_2 = Me$; R_3 = 2,4,6-tri-MePh
c, $R_1R_2 = (CH_2)_5$; R = Ph
d, $R_1 = R_2 = R_3 = Ph$
e, $R_1 = R_2 = Ph$; R_3 = *p*-ClPh

The substituted acetophenone O-benzoyl oximes represented by formulas **1b–g** reacted like **1a** with sodium hydride to give Neber rearrangement products (**3a** from **1b, c**; **3b** from **1d, f, g**; **3c** from **1e**) and substituted 4-benzoyl-3,5-diphenylisoxazoles (**5b** from **1b**, **5c** from **1c**, etc.). Propiophenone O-benzoyl oxime (**9a**), acetophenone O-(2,4,6-trimethylbenzoyl) oxime (**9b**), and cyclohexanone O-benzoyl oxime (**9c**) evolved approximately equimolar amounts of hydrogen with sodium hydride and gave derivatives of Neber rearrangement products (**3d** from **9a**, **3a** from **9b**) but no substituted isoxazoles corresponding to **5**. The acid-soluble product (2-aminocyclohexanone) from **9c** polymerized too readily to permit direct benzoylation but was identified by catalytic hydrogenation of the acid solution followed by benzoylation to yield *dl-cis*-2-benzoylaminocyclohexanol. Benzophenone O-benzoyl oxime (**9d**) and benzophenone O-(*p*-chlorobenzoyl) oxime (**9e**) did not react with sodium hydride in boiling toluene.

The mechanism[3] of the Neber rearrangement is well established and satisfactorily accounts for the amino ketone derivatives obtained in this study. Conversion of **4** (prepared[5] from α-azidostyrene) was demonstrated to occur under our experimental conditions.

The complete mechanism for formation of benzoyldiphenylisoxazoles is not apparent from the available information, but must involve successive intermolecular Claisen-type benzoylations of acetophenone O-benzoyl oximes. Support for this view is provided by the fact that a mixture of **9b** and **9e** reacted with sodium hydride to form **5b** although neither **9b** nor **9e** alone formed an isoxazole. A mixture of **1a** and **9e** also produced **5b**. The absence of isoxazoles in the products from **9a** and **9c** indicates that isoxazole formation is restricted to derivatives of methylketoximes. The stoichiometry of isoxazole formation undoubtedly entails reaction of 3 moles of **1a** with 3 moles of sodium hydride to produce 1 mole of **5a**, 1 mole of sodium benzoate, 2 moles of the sodium salt of acetophenone oxime, and 3 moles of hydrogen.

The yields of Neber rearrangement products were 3–7% from **1a–g** and 12–16% from **9a–c**. Yields of benzoyldiphenylisoxazoles from **1a–g** were 40–55%. Yields of benzoic acids were 0.4–0.6 mole per mole of **1a–g**, and 0.9–1.0 mole per mole of **9a–c**. Yields of oximes yere 0.35–0.45 mole per mole of **1a–c**. The steam-distillation procedure for isolating oximes from reaction mixtures was inefficient because of low volatility of the oximes and was applied only to products from **1a–c**. The amount of unidentified tar was greater in runs with **9a–c** than with **1a–g**.

Experimental Section[6]

Oximes from Ketones.—The ketones (0.2 mole) in 40 ml of ethanol were stirred and refluxed for 40 min with hydroxylamine sulfate (20 g, 0.12 mole) and sodium hydroxide (10 g, 0.25 mole) in 100 ml of water. The reaction mixtures were diluted with water, extracted into ether, and dried, the ether was removed, and the oximes were crystallized from petroleum ether (bp 40–60°). Melting points agreed well with accepted[7] values: acetophenone oxime, mp 57–59°; propiophenone oxime, mp 50–53°; cyclohexanone oxime, mp 89–90°; 4′-chloroacetophe-

(5) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

(6) Melting points are corrected. Semimicro analyses were performed by the authors. Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord, using KBr pellets for solids. Nmr spectra were obtained with a Varian A-60 spectrometer, using carbon disulfide (sometimes warm to promote solubility) as solvent and tetramethylsilane as an internal reference.

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956.

none oxime, mp 91–93°; 4′-methylacetophenone oxime, mp 87–88°; benzophenone oxime, mp 141–142° (from ethanol).

O-Benzoyl Oximes from Oximes.—The oximes (0.074 mole) were dissolved in 15 ml of dry pyridine and the benzoyl chloride (0.074 mole) was added dropwise with constant stirring. The mixture became hot from heat of reaction and stirring was continued until the temperature fell below 30°. Water (100 ml) was added; the O-benzoyl oximes were filtered off, dried, and crystallized from ethanol. Yields were 70–95%. The infrared spectra of **1a–g** and **9a–e** showed absorption at (±0.05 μ) 5.75, 6.25, 8.0, and 9.3–9.5 μ.

Acetophenone O-benzoyl oxime (**1a**) had mp 98–100° (lit.[8] mp 100–102°).

Cyclohexanone O-benzoyl oxime (**9c**) had mp 63–64° (lit.[9] mp 62–63°).

Benzophenone O-benzoyl oxime (**9d**) had mp 97–100° (lit.[9] mp 100°).

Acetophenone O-(*p*-chlorobenzoyl) oxime (**1b**) had mp 107–109°.

Anal. Calcd for $C_{15}H_{12}NO_2Cl$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.91; H, 4.52; N, 5.14.

Acetophenone O-(*p*-methylbenzoyl) oxime (**1c**) had mp 116–118°.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.73; H, 6.01; N, 5.58.

4′-Chloroacetophenone O-benzoyl oxime (**1d**) had mp 107–108°.

Anal. Calcd for $C_{15}H_{12}NO_2Cl$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.80; H, 4.48; N, 5.14.

4′-Methylacetophenone O-benzoyl oxime (**1e**) had mp 89–91°.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.78; H, 6.16; N, 5.56.

4′-Chloroacetophenone O-(*p*-chlorobenzoyl) oxime (**1f**) had mp 150–152°.

Anal. Calcd for $C_{15}H_{11}Cl_2NO_2$: C, 58.46; H, 3.60. Found: C, 58.26; H, 3.56.

4′-Chloroacetophenone O-(*p*-methylbenzoyl) oxime (**1g**), mp 151–152.5°.

Anal. Calcd for $C_{16}H_{14}ClNO_2$: C, 66.79; H, 4.90. Found: C, 66.23; H, 4.77.

Propiophenone O-benzoyl oxime (**9a**), mp 52–53° (from ethyl ether at −78°).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97. Found: C, 75.84; H, 5.96.

Acetophenone O-(2,4,6-trimethylbenzoyl) oxime (**9b**) had mp 99–100°.

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.72; H, 6.85.

Benzophenone O-(*p*-chlorobenzoyl) oxime (**9e**), mp 118–120°.

Anal. Calcd for $C_{20}H_{14}ClNO_2$: C, 71.54; H, 4.20. Found: C, 71.31; H, 4.19.

Reaction of O-Benzoyl Oximes with Sodium Hydride.—The reaction was conducted in a 125-ml erlenmeyer flask fitted with a magnetic stirring bar almost equal in length to the diameter of the flask bottom. Acetophenone O-benzoyl oxime (**1a**, 3.60 g, 15 mmoles) was placed in the flask with 15 ml of toluene. Sodium hydride[10] (0.69 g of 57% NaH in mineral oil, 16 mmoles) was washed twice with 5-ml portions of toluene (by stirring, centrifuging, and decanting) and transferred to the reaction flask by gentle suction through a glass tube with the aid of two 5-ml portions of toluene. The flask was attached through a reflux condenser to a 500-ml gas buret, stirred, and heated in an oil bath maintained at 115–120° for 90 min. The volume of gas (H_2) evolved was 300 ml (13.2 mmoles) after correction for toluene vapor in the flask (114 ml, determined independently), water vapor in the gas buret, and room temperature and pressure (a factor of approximately 0.88). The reaction mixture was cooled to room temperature, stirred for 5 min with 12 ml of 3 *M* hydrochloric acid, cooled, 30 ml of ether was added, and stirring was continued for 30 min. The water layer (solution A) was saved for isolation of **3a**. The ether layer was washed with water, extracted with 15 ml of 1 *M* sodium carbonate (solution B), and rewashed with water; solvent was removed by distillation, finally at reduced pressure from a boiling-water bath. Ethanol (6 ml) was added to the residue, the mixture heated to boiling, and the solution allowed to crystallize. There was obtained 0.75 g (2.3 mmoles) of **5a**, light yellow crystals mp 153–155°.

Solution A (see above) was washed with ether, benzoyl chloride (25 drops, 0.7 g) was added, the mixture was stirred vigorously, and 30 ml of 1 *M* sodium carbonate was added slowly. After 30 min of stirring ether (10 ml) was added and vigorous stirring continued for 5 min. The mixture was cooled in ice and filtered and the solid washed with water and cold ether. There was obtained 0.14 g (0.59 mmole) of **3a**, white solid, mp 123–124°.

Solution B (see above) was acidified with hydrochloric acid, the resulting precipitate dissolved in ether, the ether solution dried, and solvent removed to yield benzoic acid (0.90 g, 7.4 mmoles), mp 121–123°, confirmed by infrared spectrum.

The alcoholic mother liquor from which **5a** crystallized (see above) was added to 1.2 l. of water and distilled until 1 l. of distillate was collected. The distillate was extracted with ether, the ether solution dried, and solvent removed to yield acetophenone oxime (0.78 g, 5.7 mmoles), mp 55–59°, confirmed by infrared spectrum.

The substituted acetophenone O-benzoyl oximes **1b–g** reacted with sodium hydride and products were isolated as described for **1a**. Yields of products were not significantly different from those obtained with **1a**.

The benzoyldiphenylisoxazoles (**5a–g**) were purified by sublimation *in vacuo* and recrystallization prior to analysis, and all were colorless when pure. Recrystallization was from ethanol unless otherwise specified below. The infrared spectra of **5a–g** showed strong to medium absorption at (±0.05 μ) 6.05, 7.1, 7.6, 10.5, and 11.05 μ. The nmr spectra of **5a–g** showed the benzenoid protons as multiplets between 6.8 and 7.8 ppm, and methyl protons (when present) at (±0.02 ppm) 2.31 ppm.

4-Benzoyl-3,5-diphenylisoxazole (**5a**), mp 153–155°, was obtained from **1a**.

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31; mol wt, 325. Found: C, 81.55; H, 4.68; N, 4.46; mol wt, 328 (Signer, in acetone).

4-(*p*-Chlorobenzoyl)-5-(*p*-chlorophenyl)-3-phenylisoxazole (**5b**), mp 191–192° (from toluene[11]), was obtained from **1b**.

Anal. Calcd for $C_{22}H_{13}Cl_2NO_2$: C, 67.02; H, 3.32; N, 3.55. Found: C, 67.11; H, 3.35; N, 3.39.

4-(*p*-Methylbenzoyl)-5-(*p*-methylphenyl)-3-phenylisoxazole (**5c**), mp 136–138°, was obtained from **1c**.

Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42. Found: C, 81.28; H, 5.64.

4-Benzoyl-3-(*p*-chlorophenyl)-5-phenylisozazole (**5d**), mp 135–136°, was obtained from **1d**.

Anal. Calcd for $C_{22}H_{14}ClNO_2$: C, 73.44; H, 3.92; N, 3.89. Found: C, 73.02; H, 3.88; N, 3.84.

4-Benzoyl-3-(*p*-methylphenyl)-5-phenylisoxazole (**5e**), mp 134–135°, was obtained from **1e**.

Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.40; H, 4.97; N, 4.15.

4-(*p*-Chlorobenzoyl)-3,5-bis(*p*-chlorophenyl)isoxazole (**5f**), mp 189–190° (from toluene[11]), was obtained from **1f**.

Anal. Calcd for $C_{22}H_{12}Cl_3NO_2$: C, 61.64; H, 2.82. Found: C, 61.45; H, 3.01.

3-(*p*-Chlorophenyl)-4-(*p*-methylbenzoyl)-5-(*p*-methylphenyl)-isoxazole (**5g**), mp 135–136°, was obtained from **1g**.

Anal. Calcd for $C_{24}H_{18}ClNO_2$: C, 74.32; H, 4.68. Found: C, 74.09; H, 4.72.

Hydrogen was evolved and both acid and base-soluble products were formed from the reactions of **9a–c** with sodium hydride but only oximes (no isoxazoles) could be isolated from the neutral portion of the reaction mixtures.

Phenacylbenzamides **3a–d** were purified by crystallization from CCl_4. The infrared spectra of **3a–d** showed medium to strong absorption at (±0.02 μ) 2.91, 5.93, 6.11, and 8.20 μ. Percentage yields shown below have been calculated on the basis of 1 mole of phenacylbenzamide from 1 mole of O-benzoyl oxime.

N-Phenacylbenzamide (**3a**), mp 122–123° (lit.[12,13] mp 124°), was obtained from **1a** (4%), **1b** (3%), **1c** (6%), and **9b** (16%).

N-(*p*-Chlorophenacyl)benzamide (**3b**), mp 157–159° (lit.[13] mp 160°), was obtained from **1d** (7%), **1f** (5%), and **1g** (6%).

(8) L. Gass and F. W. Bope, *J. Am. Pharm. Assoc., Sci. Ed.*, **48**, 186 (1959).

(9) K. D. Kopple and J. J. Katz, *J. Org. Chem.*, **24**, 1976 (1959).

(10) Sodium hydride was obtained from Metal Hydrides, Inc., Beverly, Mass. It was analyzed by adding excess ethanol to a toluene suspension and measuring the volume of hydrogen evolved.

(11) Compounds **5b** and **5f** were surprisingly insoluble in ethanol and ether. In the preparations of **5b** and **5f** the products partially crystallized during the first stage of the work-up and were collected at this point.

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N-(*p*-Methylphenacyl)benzamide (**3c**), mp 112–113° (lit.[12,13] mp 114, 118°), was obtained from **1e** (3%).

N-(α-Methylphenacyl)benzamide (**3d**), mp 104–105° (lit.[14] mp 104–105°), was obtained from **9a** (16%).

Treatment of the acidic water layer (solution A above) from the work-up of **9c** with benzoyl chloride and sodium carbonate did not give a purifiable product. However, shaking the acidic solution with hydrogen (45 psi for 1 hr) and a palladium catalyst (0.1 g of 5% on charcoal) prior to treatment with benzoyl chloride and base gave a product (0.4 g) which crystallized from an ethanol–water mixture and melted at 180–183°. This product was identified as *dl-cis*-2-benzoylaminocyclohexanol by comparison of the infrared spectrum with that of a sample prepared by established procedures[15]—the spectra were identical and different from the spectrum of the *trans* isomer prepared[15] from epoxycyclohexane and ammonia. The earlier workers[15] reported mp 184–186° (from ethyl acetate) and 193° (from ligroin) for *dl-cis*-2-benzoylaminocyclohexanol but we found mp 180–183° (from ethanol–water) for the product prepared by their method.

Acids obtained from the carbonate extracts (solution B above) were characterized by melting point and infrared spectra. Yields reported below have been calculated on the basis of a mole of acid from a mole of O-benzoyl oxime. Benzoic acid was obtained from **1a** (49%), **1d** (44%), **1e** (47%), **9a** (95%), and **9c** (43%). *p*-Chlorobenzoic acid was obtained from **1b** (50%), and **1f** (47%). *p*-Toluic acid was obtained from **1c** (54%) and **1g** (58%). 2,4,6-Trimethylbenzoic acid was obtained from **9b** (90%).

Reaction of Mixed 9b–9e and 1a–9e with Sodium Hydride.—Sodium hydride (16 mmoles) was added to 1.41 g (5 mmoles) of acetophenone O-(2,4,6-trimethylbenzoyl) oxime (**9b**) and 3.36 g (10 mmoles) of benzophenone O-(*p*-chlorobenzoyl) oxime (**9e**) in 15 ml of toluene. The reaction and work-up were carried out as described above except that 25 ml (instead of 6 ml) of ethanol was added to the neutral residue after removal of solvent and the hot solution was seeded with **5b**. Crystals which formed in the warm solution were filtered and washed with hot ethanol. These crystals (mp 190–192°, 0.30 g) were confirmed as **5b** by infrared spectrum. Concentration and cooling of the mother liquor from crystallization of **5b** gave a solid, mp 131–135°, judged to be mainly benzophenone oxime on the basis of infrared spectrum. Hydrogen evolved during the reaction amounted to 190 ml (8.5 mmoles). The acidic water layer (solution A) yielded 0.25 g of **3a**, mp 121–123°, confirmed by infrared spectrum.

Repetition of the above experiment with substitution of 5 mmoles of **1a** for **9b** gave the same products in practically the same yields.

3,5-Diphenylisoxazoles (6a–g) from 4-Benzoyl-3,5-diphenylisoxazoles.—A stock solution was prepared by dissolving 2.4 g of potassium hydroxide in 2 ml of water, adding 20 ml of 2,2′-oxydiethanol and heating to 160° to expel water. A portion (2 ml) of the stock solution was placed in a small test tube with 0.2 g of **5a** (or **5b**, etc) and the tube placed in an oil bath maintained at 150°. The solution was stirred until homogeneous and heated for 30 min thereafter. The reaction mixture was diluted with water and extracted with ether. The ether solution was washed with water, dilute hydrochloric acid, and water and dried and the ether removed. Crystallization of the residue from ethanol gave pure **6a** (or **6b**, etc.). Yields were 0.02–0.03 g.

The infrared spectra of **6a–g** showed a medium intensity peak at 10.5 μ and a series (6 for **6b**, 10 for **6c**, 7 for others) of weak to medium intensity peaks between 6.2 and 7.3 μ. The nmr spectra showed methyl protons (when present) at 2.39, the proton on the isoxazole ring at 6.62–6.68, and the benzenoid protons as multiplets between 7.0 and 7.9 ppm.

3,5-Diphenylisoxazole (**6a**), mp 141–142° (lit.[16] mp 141°), was obtained from **5a**.

5-(*p*-Chlorophenyl)-3-phenylisoxazole (**6b**), mp 175–176° (lit.[17] mp 178–179°), was obtained from **5b**.

3-Phenyl-5-*p*-tolylisoxazole (**6c**), mp 138–139° (lit.[18] mp 136–137°), was obtained from **5c**.

3-(*p*-Chlorophenyl)-5-phenylisoxazole (**6d**), mp 175–176° (lit.[19] mp 175°), was obtained from **5d**.

5-Phenyl-3-*p*-tolylisoxazole (**6e**), mp 129–130° (lit.[18] mp 125–126°), was obtained from **5e**.

3,5-Bis(*p*-chlorophenyl)isoxazole (**6f**), mp 192–194°, was obtained from **5f**.

Anal. Calcd for $C_{15}H_9Cl_2NO$: C, 62.09; H, 3.13. Found: C, 61.89; H, 3.16.

3-*p*-Chlorophenyl-5-*p*-tolylisoxazole (**6g**), mp 200–201°, was obtained from **5g**.

Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.49. Found: C, 71.10; H, 4.39.

4-Benzyl-3,5-diphenylisoxazole (8).—This compound was prepared from 4-benzoyl-3,5-diphenylisoxazole (**5a**) by a modification of method 3 of Nystrom and Berger.[20] Freshly sublimed aluminum chloride (0.3 g, 2 mmoles) was dissolved in 15 ml of anhydrous ether and 0.33 g (1 mmole) of **5a** was added. The solution was stirred and refluxed while a solution of 1 mmole of lithium aluminum hydride in ether was added dropwise. Refluxing and stirring were continued for 30 min. Dilute hydrochloric acid was added dropwise until the solution was acidic. The ether layer was washed twice with water and dried and the solvent removed. The residue crystallized from ethanol, and yielded 0.18 g of white crystals, mp 115–116°. The same compound, **8**, was also prepared from benzyldibenzoylmethane (**7c**) and hydroxylamine hydrochloride. The method of Abell[21] was used to prepare **7c**, mp 109–110° (lit.[21] mp 108°). A solution of 1.57 g of **7c**, 0.49 g of hydroxylamine hydrochloride, 1 ml of water, 0.5 ml of pyridine, and 25 ml of ethanol was refluxed for 1 hr. Solvent (22 ml) was removed by distillation; the residue was diluted with water and filtered; and the solid was crystallized from ethanol. There was obtained 1.02 g of white crystals, mp 115–116°. The identity of this product with the reduction product from **5a** was confirmed by comparison of infrared and nmr spectra. The methylene protons appeared at 4.03 ppm.

Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50. Found: C, 84.57; H, 5.62.

Reaction of Tribenzoylmethane with Hydroxylamine.—Tribenzoylmethane (**7b**) was prepared by the method of Claisen,[22] mp 245–248° (lit.[22,23] mp 228–231°, 245–250°). Hydroxylamine hydrochloride (0.25 g in 0.5 ml of water), **7b** (0.8 g), pyridine (0.25 ml), and ethanol (25 ml) were stirred and refluxed for 1 hr. Considerable solid remained undissolved. The mixture was cooled and filtered to yield 0.43 g of **7b**, identified by its melting point and infrared spectrum. Evaporation of the filtrate to small volume and recrystallization of the resulting precipitate from ethanol gave 0.1 g of crystals, mp 142–144°, infrared spectrum identical with that of **6a** prepared from **5a** or from **7a** by the procedure described for preparing **8** from **7c**.

Tribenzoylmethane did not react with hydroxylamine hydrochloride in boiling ethanol in the absence of pyridine. Use of dioxane instead of ethanol as solvent (with or without pyridine) gave homogeneous reaction mixtures but the same products.

N-Phenacylbenzamide (3a) from 3-Phenyl-2H-azirine (4).—The method of Smolinsky[5] was used to prepare **4**, bp 80° (10 mm), absorption at 5.74 μ. A solution of **4** (0.3 g) in 3 *M* hydrochloric acid (4 ml) was prepared by stirring for 30 min and treated with benzoyl chloride (0.56 g) followed by sodium carbonate solution as described above for preparation of N-phenacylbenzamides. There was obtained 0.37 g of white solid, mp 122–123°, infrared spectrum identical with that of **3a** from **1a**.

Registry No.—**1b**, 14688-23-4; **1c**, 14764-42-2; **1d**, 14688-24-5; **1e**, 14688-25-6; **1f**, 14688-26-7; **1g**, 14688-27-8; **5a**, 14688-28-9; **5b**, 14764-43-3; **5c**, 14764-44-4; **5d**, 14764-45-5; **5e**, 14688-29-0; **5f**, 14764-46-6; **5g**, 14764-47-7; **6f**, 14688-30-3; **6g**, 14688-31-4; **8**, 14688-32-5; **9a**, 14688-33-6; **9b**, 14764-48-8; **9e**, 14688-34-7; sodium hydride, 7646-69-7.

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