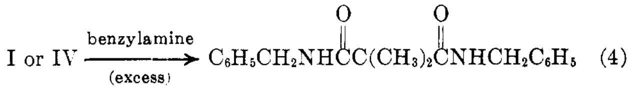
produced. Also, treatment of IV with benzylamine will produce VI (eq 4). Apparently, this reaction is



$$\text{I or IV} \xrightarrow[\text{(excess)}]{\text{benzylamine}} C_6H_5CH_2NH\overset{O}{\overset{\|}{C}}C(CH_3)_2\overset{O}{\overset{\|}{C}}NHCH_2C_6H_5 \quad (4)$$

VI

analogous to the familiar iodoform reaction of methyl ketones.

Experimental Section

Dimethylketene was prepared by the pyrolysis of the commercially available ketene dimer, tetramethyl-1,3-cyclobutanedione, and then distilled just prior to the addition reaction.[5] All of the solvents used in this study were dried by refluxing and distilling from lithium aluminum hydride through a 30-plate Oldershaw column. The pmr spectra were recorded on a Varian A-60 instrument.

4,4,4-Trichloro-2,2-dimethyl-3-ketobutanoyl Chloride. (I).—A solution of 2.6 g of dimethylketene (0.037 mol) in 25 ml of hexane was added slowly to a stirred solution of 10 ml (0.0912 mol) of trichloroacetyl chloride in 50 ml of hexane at room temperature. After standing overnight, the solvent was removed under reduced pressure, and the residue was fractionated to yield 5.7 g (61%) of I at 68–70° (0.7 mm). The spectral data were given above.

Anal. Calcd for $C_6H_6Cl_4O_2$: C, 28.55; H, 2.20. Found: C, 28.55; H, 2.10.

Methyl 4,4,4-Trichloro-2,2-dimethyl-3-ketobutanoate. (II).—A 2-g (0.0079 mol) portion of I was added dropwise with stirring to an excess of dry methanol at room temperature. The excess methanol was evaporated, and the residue was recrystallized from ligroin to yield 1.7 g (91%) of II: mp 42–43°; ir 1755 and 1740 cm^{-1}; pmr (CCl_4) a singlet at 3.75 and 1.60 ppm. The peak areas were in the ratio of 1:2.

Anal. Calcd for $C_7H_9Cl_3O_3$: C, 33.90; H, 3.63. Found: C, 33.75; H, 3.72.

4,4,4-Trichloro-2,2-dimethyl-3-ketobutanoic Acid (III).—The dropwise addition of I to an excess of water resulted in a quantitative conversion into III which was recrystallized from ligroin: mp 115–116°; ir 1710 cm^{-1}.

Anal. Calcd for $C_6H_7Cl_3O_3$: C, 30.86; H, 3.02. Found: C, 30.95; H, 2.72.

N-Benzyl-4,4,4-trichloro-2,2-dimethyl-3-ketobutanamide (IV).—A solution of 0.75 g (0.00297 mol) of I in 25 ml of dry hexane was added dropwise to a stirred solution of 0.318 g (0.00297 mol) of benzylamine in 10 ml of dry hexane. A white precipitate formed upon addition. The reaction mixture was washed with dilute hydrochloric acid solution, followed by a water wash. Drying and evaporation of the solvent yielded 0.4 g of IV. This material was recrystallized from 70% ethanol: mp 100.5–102°; ir 1745 and 1635 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}Cl_3NO_2$: C, 48.40; H, 4.34. Found: C, 48.45; H, 4.51.

N-Phenyl-4,4,4-trichloro-2,2-dimethyl-3-ketobutanamide (V).—The anilide was prepared in the same manner as described above for the N-benzamide, except ether was used as the solvent. Recrystallization from ligroin yielded crystals with mp 146–147°; ir 1745 and 1635 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}Cl_3NO_2$: C, 46.6; H, 3.89. Found: C, 46.86; H, 3.61.

N,N′-Dibenzyldimethylmalonamide (VI).—A 3.5-g (0.0139 mol) portion of I was added dropwise with stirring to a solution of 5 g (0.0467 mol) of benzylamine in 250 ml of benzene. The reaction mixture was washed with dilute hydrochloric acid solution, followed by water. The benzene solution was dried over anhydrous magnesium sulfate, filtered, and cooled to yield 3.5 g (81%) of VI. The crude product was recrystallized from 70% ethanol to yield small white needles, mp 166–167°. A mixture melting point with an authentic sample of VI prepared from dimethylmalonyl chloride and benzylamine showed no depression.

Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.50; H, 7.10; mol wt, 310. Found: C, 73.50; H, 7.18; mol wt, 310 (mass spectrum).

Compound VI could also be prepared by treatment of IV with an excess of benzylamine.

Registry No.—I, 17953-83-2; II, 17953-84-3; III, 17953-85-4; IV, 17953-86-5; V, 17953-87-6; VI, 17953-88-7; Me_2CCO, 598-26-5; Cl_3CCOCl, 76-02-8.

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(5) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

Reactions of Phenyl Isocyanate and Phenyl Isothiocyanate with Indole and Metal Derivatives of Indole

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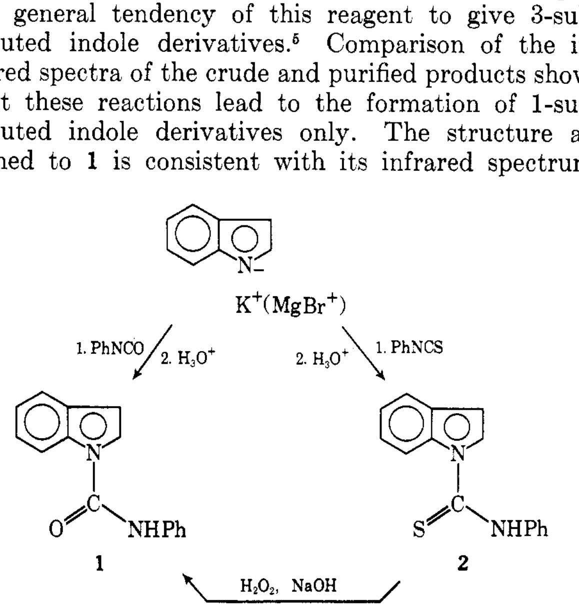
Pyrrole is known to react with phenyl isocyanate and phenyl isothiocyanate to form 2-pyrrolecarboxanilide[1] and 2-pyrrolethiocarbanilide,[2] respectively. With the same reagents, pyrrolylpotassium forms the 1-carboxanilide and 1-thiocarbanilide, whereas pyrrolylmagnesium bromide gives mixtures of the 1 and 2 derivatives.[3,4]

We wish to report now on the analogous reactions of indole, indolylpotassium, and indolylmagnesium bromide. When treated with phenyl isocyanate or phenyl isothiocyanate in tetrahydrofuran, indolylpotassium yields 1-indolecarboxanilide (1) or 1-indolethiocarbanilide (2). It is noteworthy that the same compounds are obtained from the corresponding reactions of indolylmagnesium bromide in tetrahydrofuran, despite the general tendency of this reagent to give 3-substituted indole derivatives.[5] Comparison of the infrared spectra of the crude and purified products shows that these reactions lead to the formation of 1-substituted indole derivatives only. The structure assigned to 1 is consistent with its infrared spectrum, which shows a carbonyl absorption at 1710 cm^{-1}, but not the characteristic indole N–H band in the 3400–3500-cm^{-1} region.[6] Furthermore, alkaline hydrolysis of 1 yields a mixture of indole and aniline. The structure of 2 is confirmed by its smooth oxidation to 1 with alkaline hydrogen peroxide.



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(1) A. Treibs and W. Ott, *Ann.*, **577**, 119 (1952).

(2) E. Bullock and R. J. Abraham, *Can. J. Chem.*, **37**, 1391 (1959).

(3) E. P. Papadopoulos and H. S. Habiby, *J. Org. Chem.*, **31**, 327 (1966).

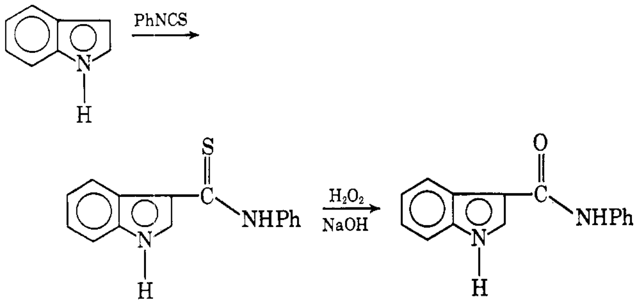
(4) E. P. Papadopoulos, *ibid.*, **31**, 3060 (1966).

(5) M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," Edward Arnold Ltd., London, England, 1967, p 324.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1962.

When a mixture of equimolar amounts of indole and phenyl isocyanate is allowed to stand at room temperature for several hours, a solid mass is obtained, which, however, does not contain any of the 1-, 2-, and 3-indolecarboxanilides. So far, we have been unable to determine the nature of this product, purification of which is made difficult by its low solubility in the common solvents. The 2- (**3**), and the 3-indolecarboxanilide (**4**) have been prepared from the corresponding acids *via* the acid chlorides. The infrared spectrum of **3** has the indole N–H band at 3440 cm^{-1} and a carbonyl band at 1660 cm^{-1}; that of **4** shows corresponding absorptions at 3460 and 1655 cm^{-1}. There is good agreement between the relative positions of carbonyl absorption of N- and C-indolecarboxanilides and those of the corresponding derivatives of pyrrole[3] and imidazole.[7]

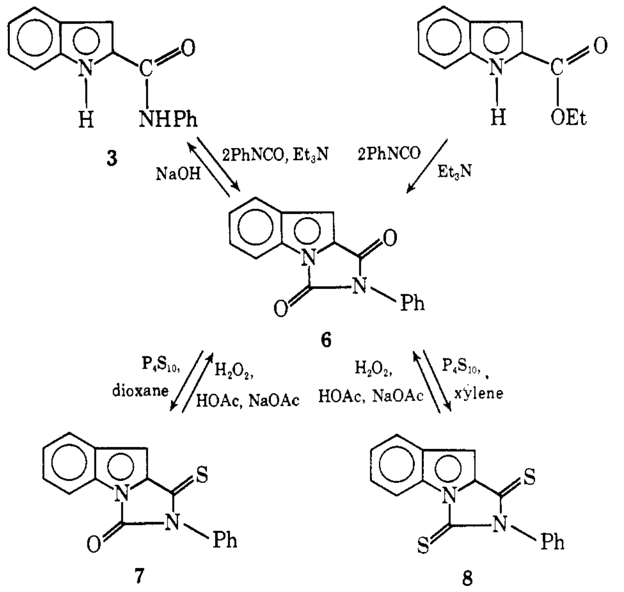
Indole reacts sluggishly with phenyl isothiocyanate to give, after prolonged heating and in low yield, a product which must be the 3-indolethiocarbanilide (**5**), as shown by its oxidation to **4** with alkaline hydrogen peroxide.



5 **4**

In complete analogy with the corresponding pyrrole derivative,[3] 2-indolecarboxanilide (**3**) reacts with phenyl isocyanate in the presence of triethylamine to form 2-phenylindolo[1,2-*c*]hydantoin (**6**) and N,N′-diphenylurea (Scheme I). The infrared spectrum of **6** shows two carbonyl bands at relatively high frequencies (1785 and 1735 cm^{-1}), consistent with the hydantoin structure[6] and in good agreement with those observed in the spectra of 2-phenylpyrrolo[1,2-*c*]hydantoin,[3] and 2,5,6-triphenylimidazo[1,2-*c*]hydantoin.[7] The structure assigned to **6** is further supported by its conversion into **3** by alkaline hydrolysis and by its formation in excellent yield from 2-ethoxycarbonylindole by the action of phenyl isocyanate and triethylamine. The two carbonyls of **6** exhibit a difference in reactivity toward phosphorus pentasulfide analogous to that observed for the corresponding pyrrole derivative.[4] Whereas refluxing with phosphorus pentasulfide in dioxane readily converts **6** into a monothiohydantoin, conversion of **6** into 2-phenylindolo[1,2-*c*]dithiohydantoin (**8**) requires prolonged refluxing of the reagents in xylene. Compared with the infrared spectrum of **6**, that of its monothio derivative retains the carbonyl absorption at higher frequency (1775 cm^{-1}), but lacks the band at lower frequency. The high frequency carbonyl absorption is consistent with the 2-phenylindolo[1,2-*c*]-1-thiohydantoin (**7**) structure, which finds its parallel in the thiohydantoin obtained in the pyrrole series by the same sequence of steps.[4] The spectrum of **8**, as expected, shows no absorption in the carbonyl region. Both **7** and **8** are oxidized to **6** by hydrogen peroxide, in the presence of acetic acid and sodium acetate.

SCHEME I



Experimental Section

Melting points were determined on a calibrated Fisher-Johns melting point apparatus. Infrared spectra were run on a Perkin-Elmer Model 257 infrared spectrophotometer.

1-Indolecarboxanilide (1). A. From Indolylpotassium.—A solution of 11.7 g (0.1 mol) of indole in 100 ml of tetrahydrofuran was stirred at reflux with 3.9 g (0.1 g-atom) of potassium until all the metal had reacted. To the resulting solution of indolylpotassium, diluted with 100 ml of tetrahydrofuran and cooled to room temperature, was added dropwise over 0.5 hr 11.9 g (0.1 mol) of phenyl isocyanate dissolved in 100 ml of tetrahydrofuran. After the reaction mixture had been stirred at room temperature for an additional 15 hr, the solvent was removed by distillation under reduced pressure and the residue was cooled and treated with 200 ml of water. Acidification with dilute hydrochloric acid and filtration yielded 24.0 g of crude product, which was recrystallized from petroleum ether (bp 100–115°) to give 13.2 g (56%) of 1-indolecarboxanilide (**1**), mp 121–123°. Upon further recrystallization the melting point became 124–125°.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.38; H, 5.13; N, 11.96.

B. From Indolylmagnesium Bromide.—Indolylmagnesium bromide was prepared by dropwise addition of 11.7 g (0.1 mol) of indole dissolved in 50 ml of tetrahydrofuran to a solution of ethylmagnesium bromide made from 13.6 g (0.125 mol) of ethyl bromide and 2.4 g (0.1 g-atom) of magnesium in 100 ml of tetrahydrofuran. A solution of 10.8 g (0.09 mol) of phenyl isocyanate in 50 ml of tetrahydrofuran was introduced dropwise (0.5 hr) into the stirred reaction mixture, and the resulting solution was stirred at room temperature for 17 hr. Hydrolysis with 50 ml of water containing 10.7 g of ammonium chloride was followed by separation of the layers and extraction of the aqueous layer with ether. The combined organic solutions were treated with animal charcoal and dried over anhydrous magnesium sulfate. Evaporation of the solution under reduced pressure yielded 20.7 g of crude product, which was recrystallized from methyl alcohol to give 9.8 g of **1**, mp 122.5–124.5°, as a first crop, and 2.1 g, mp 121.5–122.5°, as a second (total yield 56%). The infrared spectra of the crude and the pure product of this reaction, respectively, were the same as those of the preceding preparation. There was no melting point depression on admixture of the two pure products.

Hydrolysis of 1-Indolecarboxanilide.—To a solution of 0.5 g of **1** in 15 ml of ethyl alcohol was added 2 g of potassium hydroxide dissolved in 5 ml of water and the mixture was refluxed for 3 hr.

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(7) R. Gompper, E. Hoyer, and H. Herlinger, *Ber.*, **92**, 550 (1959).

Cooling of the solution was followed by ether extraction and evaporation of the extract to a small volume. Gas-liquid partition chromatography showed that the extract contained equimolar quantities of indole and aniline.

1-Indolethiocarbanilide (2). A. From Indolylpotassium.—A solution of 13.5 g (0.1 mol) of phenyl isothiocyanate in 100 ml of tetrahydrofuran was added dropwise over 0.5 hr to a stirred solution of indolylpotassium prepared as described earlier from 3.9 g (0.1 g-atom) of potassium and 11.7 g (0.1 mol) of indole in 200 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature for 15 hr, the solvent was removed by distillation under reduced pressure, and the residue was dissolved in 200 ml of water. The resulting solution was washed with ether and was acidified with dilute hydrochloric acid to yield 20 g of crude 1-indolethiocarbanilide (2), mp 125–127°. Evaporation of the ether washings to dryness, treatment of the residue with petroleum ether (bp 40–80°), and recrystallization from 95% ethyl alcohol afforded a further 1.7 g of product, mp 125.5–128.5 (total yield 86%). Recrystallization from 95% ethyl alcohol gave pale yellow crystals of the pure compound melting at 128–129°.

Anal. Calcd for $C_{15}H_{12}N_2S$: C, 71.41; H, 4.80; N, 11.11; S, 12.69. Found: C, 71.57; H, 4.70; N, 11.16; S, 12.73.

B. From Indolylmagnesium Bromide.—Indolylmagnesium bromide was prepared as described earlier from 11.7 g (0.1 mol) of indole, 2.4 g (0.1 g-atom) of magnesium, and 13.6 g (0.125 mol) of ethyl bromide in a total of 150 ml of tetrahydrofuran. After dropwise introduction of a solution of 10.5 g (0.09 mol) of phenyl isothiocyanate in 100 ml of tetrahydrofuran, the reaction mixture was stirred at room temperature for 21 hr. Hydrolysis with aqueous ammonium chloride and the usual work-up yielded 16.2 g of crude product, which was recrystallized from 95% ethyl alcohol to give 13.4 g (59%) of 2, mp 125–127°. The infrared spectra of the crude and the purified product of this reaction were identical with those of the preceding one, and no melting point depression was observed upon admixture of the two pure products.

Oxidation of 1-Indolethiocarbanilide (2) to 1-Indolecarboxanilide (1).—An ice-cold solution of 1 g of 2 and six pellets of sodium hydroxide in 35 ml of ethyl alcohol and 2 ml of water was mixed with 6 ml of hydrogen peroxide (30%) and the mixture was kept at 0° for 1 hr and, subsequently, in a refrigerator overnight. Dilution with water yielded 0.8 g of a solid, mp 122–123°, the infrared spectrum of which was identical with that of 1. One recrystallization from ethyl alcohol raised the melting point to 123.5–125°, and a mixture with authentic 1 melted at 124–125°.

2-Indolecarboxanilide (3).—A mixture of 4.0 g (0.025 mol) of 2-indolecarboxylic acid and 5.0 g (0.042 mol) of thionyl chloride was heated at 70–75° for 4 hr. After the excess of thionyl chloride had been removed by distillation under reduced pressure, the residue was treated with two 20-ml portions of petroleum ether (bp 40–80°), and each time was evaporated under reduced pressure. The final residue was treated with 300 ml of ether and the resulting solution of the acid chloride was filtered into a solution of 10 g of aniline in 100 ml of ether. The mixture was allowed to stand for 2 hr, then it was filtered, and the filtrate was washed successively with water, dilute hydrochloric acid, water, aqueous sodium bicarbonate, and water. After treatment with animal charcoal and anhydrous magnesium sulfate, the ether solution was evaporated to dryness under reduced pressure to yield 4.0 g (68%) of 2-indolecarboxanilide (3), mp 198–202°. Recrystallization from 95% ethyl alcohol raised the melting point to 202–203°.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.14; H, 5.04; N, 11.91.

3-Indolecarboxanilide (4).—Starting with 4.0 g of 3-indolecarboxylic acid and following the procedure described for the preparation of 3, there was obtained 4.5 g (76%) of 3-indolecarboxanilide (4), mp 176.5–177.5°. After recrystallization from 50% ethyl alcohol, the pure compound melted at 178.5–179.5°.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.05; H, 5.12; N, 11.73.

3-Indolethiocarbanilide (5).—A mixture of 11.7 g (0.1 mol) of indole and 13.5 g (0.1 mol) of phenyl isothiocyanate was heated at 80–90° for 8 days. The dark, tarry product was refluxed with 100 ml of petroleum ether (bp 100–115°) and the resulting solid residue was recrystallized from 95% ethyl alcohol to yield 9.7 g (38%) of crude product, mp 180–185°. Further recrystallization from 95% ethyl alcohol gave pure 3-indolethiocarbanilide (5), yellow crystals, mp 188–189°.

Anal. Calcd for $C_{15}H_{12}N_2S$: C, 71.41; H, 4.80; N, 11.11; S, 12.69. Found: C, 71.53; H, 4.85; N, 10.97; S, 12.83.

Oxidation of 3-indolethiocarbanilide (5) to 3-indolecarboxanilide (4) was run as described for the oxidation of 2 to 1, except that the alcoholic solution of the product was allowed to stand at room temperature for 0.5 hr prior to its dilution with water. From 1 g of 5 there was obtained 0.8 g of 4, mp 178–180°, raised to 178.5–180° by recrystallization from 50% ethyl alcohol. There was no melting point depression upon admixture with an authentic sample of 4.

2-Phenylindolo[1,2-*c*]hydantoin (6). A. From 2-Indolecarboxanilide (3).—A mixture of 2.4 g (0.01 mol) of 3, 2.4 g (0.02 mol) of phenyl isocyanate, and 3 ml of triethylamine was heated at 90° for 2 hr. The solid product was cooled, washed with petroleum ether (bp 40–80°), and mixed thoroughly with 150 ml of chloroform. Filtration of the mixture yielded 1.9 g of a solid, mp 238–240°, identified as N,N′-diphenylurea on the basis of its infrared spectrum and a mixture melting point with an authentic sample. Evaporation of the chloroform solution under reduced pressure gave 2.5 g of solid material, which was recrystallized from *n*-propyl alcohol to yield 1.9 g (72%) of 2-phenylindolo[1,2-*c*]hydantoin (6), mp 212–213°.

Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.46; H, 3.78; N, 10.71.

B. From 2-Ethoxycarbonylindole.—A mixture of 2.4 g (0.0125 mol) of 2-ethoxycarbonylindole, 3.0 g (0.025 mol) of phenyl isocyanate, and 1.5 ml of triethylamine was heated at 100° for 4 hr. Cooling and washing of the solid product with four 10-ml portions of ethyl alcohol yielded 3.0 g (91%) of a solid, mp 211–213°, the infrared spectrum of which was identical with that of 6 obtained from the preceding reaction. There was no melting point depression when the products of the two reactions were mixed.

Hydrolysis of 2-Phenylindolo[1,2-*c*]hydantoin (6).—A mixture of 0.2 g of 6, 1 ml of 10% aqueous sodium hydroxide, and 4 ml of ethyl alcohol was heated for a few moments, until the original yellowish solid had gone into solution and a colorless precipitate had started forming. Cooling and dilution with water yielded 0.1 g of a solid, mp 202–204°, identified as 2-indolecarboxanilide (3) on the basis of its infrared spectrum and a mixture melting point with authentic 3.

2-Phenylindolo[1,2-*c*]-1-thiohydantoin (7).—To a solution of 1 g of 6 in 30 ml of dioxane 2 g of phosphorus pentasulfide was added and the mixture was refluxed for 4 hr. After addition of a further 2 g of phosphorus pentasulfide, refluxing was continued for an additional 4 hr. Filtration of the hot mixture and removal of the solvent by distillation under reduced pressure gave a dark residue, which was refluxed with 100 ml of petroleum ether (bp 100–115°). A new filtration of the hot mixture yielded a solution, evaporation of which gave 0.6 g of crude product, mp 168–173°. After several recrystallizations from 95% ethyl alcohol, there was obtained pure 2-phenylindolo[1,2-*c*]-1-thiohydantoin (7), orange-red crystals, mp 182–183°.

Anal. Calcd for $C_{16}H_{10}N_2OS$: C, 69.06; H, 3.62; N, 10.07; S, 11.50. Found: C, 69.20; H, 3.51; N, 10.08; S, 11.48.

Oxidation of 2-Phenylindolo[1,2-*c*]-1-thiohydantoin (7) to 2-Phenylindolo[1,2-*c*]hydantoin (6).—A mixture of 0.3 g of 7, 3 ml of acetic acid, 0.3 g of sodium acetate, and 2 ml of hydrogen peroxide (30%) was stirred at room temperature for 24 hr.[8] The addition of hydrogen peroxide was repeated twice, followed each time by a 24-hr stirring period. Dilution with water gave a precipitate which was separated by filtration and washed with water to give 0.1 g of product, mp 205–209°, the infrared spectrum of which was identical with that of 6.

2-Phenylindolo[1,2-*c*]dithiohydantoin (8).—A mixture of 0.6 g of 6, 2.4 g of phosphorus pentasulfide, and 20 ml of xylene was refluxed for 36 hr. After filtration of the hot mixture, the solvent was removed by distillation under reduced pressure and the residue was refluxed with 50 ml of petroleum ether (bp 100–115°). Evaporation of the extract to dryness yielded 0.5 g of crude product, mp 185–188°. After several recrystallizations from 95% ethyl alcohol, the melting point of pure 2-phenylindolo[1,2-c]dithiohydantoin (8), dark purple crystals, was 195–196°.

Anal. Calcd for $C_{16}H_{10}N_2S_2$: C, 65.30; H, 3.43; N, 9.52; S, 21.75. Found: C, 65.36; H, 3.41; N, 9.35; S, 21.61.

Oxidation of 2-Phenylindolo[1,2-*c*]dithiohydantoin (8) to 2-Phenylindolo[1,2-*c*]hydantoin (6).—The reaction was run as

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[8] G. Bianchetti, P. Dalla Croce, and D. Pocar, *Gazz. Chim. Ital.*, **94**, 606 (1964).

described for the conversion of **7** into **6**. From 0.2 g of **8**, 2 ml of acetic acid, 0.2 g of sodium acetate, and a total of 6 ml of hydrogen peroxide (30%) there was obtained 0.1 g of product, mp 208–210°, the infrared spectrum of which was identical with that of **6**.

Registry No.—**1**, 16036-21-8; **2**, 17954-04-0; **3**, 17954-05-1; **4**, 17954-06-2; **5**, 6954-17-2; **6**, 17954-08-4; **7**, 17954-09-5; **8**, 17954-10-8; PhNCO, 103-71-9; PhNCS, 103-72-0; indole, 102-72-9.

Acknowledgment.—This work was supported by a grant from the Arts and Sciences Research Committee of the American University of Beirut, Beirut, Lebanon. The authors are grateful to Dr. C. H. Issidorides for his constant help and encouragement.

Nitrosoazomethine Derivatives. Oxidation of Amidoximes[1]

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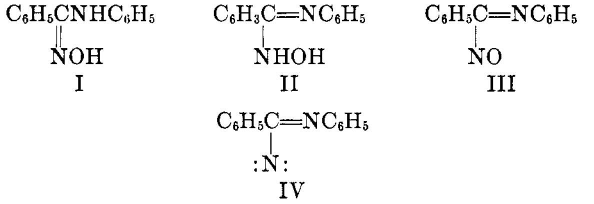
Received July 1, 1968

To investigate deoxygenation of nitrosoazomethine derivatives (III) as a method for the generation of azomethine nitrenes (IV), a preparation of these virtually unknown nitroso compounds[2a] by the oxidation and dehydrogenation of secondary amidoximes has been sought.



$C_6H_5C(=NOH)NHC_6H_5$ I

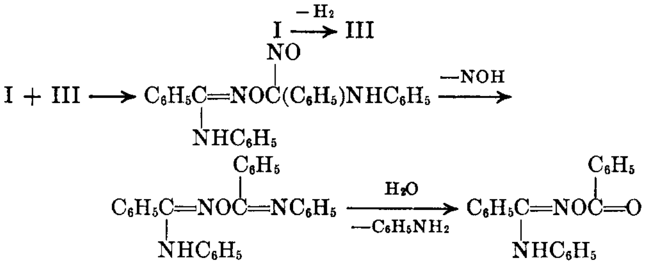
$C_6H_5C(=NC_6H_5)NHOH$ II

$C_6H_5C(=NC_6H_5)NO$ III

$C_6H_5C(=NC_6H_5)\ddot{N}{:}$ IV

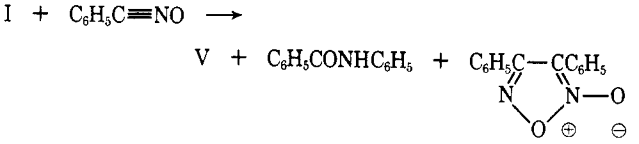
At room temperature or below, the oxime (I) of benzanilide reacts readily with lead tetraacetate, N-bromosuccinimide, or diethyl azodicarboxylate. The O-benzoyl derivative (V) of the oxime of benzanilide is produced in yields of 15.6, 13, and 57.7%, respectively. Its formation is consistent with an initial oxidation or dehydrogenation of the amidoxime into 1,2-diphenyl-2-nitrosoazomethine (III) and subsequent condensation between I and III followed by hydrolysis during the work-up (Scheme I).

SCHEME I



As alternative reactions leading to the formation of V, the condensation of I with either itself or benzanilide at the temperatures employed was eliminated by separate experiments which revealed no reaction in either event. A small amount of benzanilide isolated from each oxidation or dehydrogenation may be attributed to hydrolysis of anyone of the several derivatives of $C_6H_5C(NHC_6H_5){=}N{-}$ which may be present during work-up of the reaction mixture.

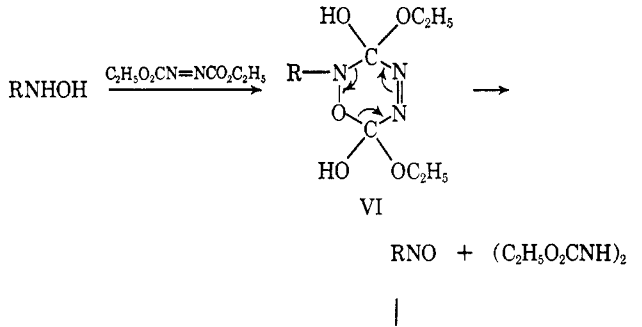
An independent synthesis of V (75.6% yield) was developed from a new reaction between benzonitrile oxide and the oxime (I). In addition to V, benzanilide



and diphenylfuroxan were formed. Although there is no direct positive evidence to support it, the possibility that benzonitrile oxide may be generated during an oxidation of I has been recognized.

Both oxidation and dehydrogenation may proceed from the tautomeric hydroxylamine (II). Facile oxidation of hydroxylamines to nitroso compounds is well established; however, dehydrogenation of the hydroxylamino function by ethyl azodicarboxylate was unknown heretofore. By this reagent phenylhydroxylamine has been dehydrogenated to nitrosobenzene in 71% yield.[2b] An explanation for the reaction is based upon a concerted or stepwise dissociation of a proposed cyclic adduct, VI (Scheme II). Ethyl hydrazocarboxylate is produced in a comparable yield of 72%. Conceivably this new preparation of a nitroso compound may be of value when carried out in the presence of other groups sensitive to oxidizing or reducing reagents. Closely related dehydrogenation of other compounds, *e.g.*, primary and secondary alcohols and primary amines and mercaptans, by diethyl azodicarboxylate has been reported.[3]

SCHEME II



In low yield a by-product, 3,4-diphenyl-1,2,4-oxadiazolone-5 (VII), is also formed in the reaction between I ⇌ II and ethyl azodicarboxylate. It was independ-

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[2] (a) P. A. S. Smith ["Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, Pasadena, California, 1966] discusses nitrosolic acids, $RC(NO){=}NOH$ (pp 356 and 384) and $CH_3C({=}NOH)N(OH)N{=}C(NO)CH_3$ (p 92). J. H. Boyer in "Heterocyclic Compounds," R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, Vol. 7, p 428] discusses $CH_3N(C_6H_5)$-$N{=}C(CH_3)NO$. (b) Our work on the dehydrogenation of phenylhydroxylamine was carried out before a similar report appeared: E. C. Taylor and F. Yoneda, *Chem. Commun.*, 199 (1967).

[3] F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966).