

The salt was decomposed in alcoholic sodium bicarbonate solution and the base was recovered as an oil from ether. Nmr spectrum (CDCl₃) showed ind-NH 8.2, ind- α -H 6.95 ppm.

2,3-Dimethyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (4e).—**3e** hydrochloride, 0.43 g, suspended in 4.3 ml of 1 *N* hydrochloric acid was held on steam for 1 hr during which time hydrogen cyanide was evolved and cottony crystals replaced the original salt. The suspension was chilled and 0.35 g (89%) of salt was recovered. It was recrystallized from water, mp 295°.

Anal. Calcd for C₁₇H₂₁ClN₂: Cl, 12.28. Found: Cl, 12.25.

The salt was decomposed in sodium bicarbonate solution containing alcohol and the base was recovered from ether. Recrystallized from alcohol it had vac mp 192–193°, with a slight sinter at 93°; mass spectrum *m/e* 252 (M⁺) 170; nmr (CDCl₃) Me 1.68 ppm (6 H).

Anal. Calcd for C₁₇H₂₀N₂: C, 80.91; H, 7.99. Found: C, 81.10; H, 7.73; loss on drying, 3.34.

6-Cyano-4-methyl-1-(2-indol-3-ylethyl)-1,2,5,6-tetrahydropyridine (3f).—**1f**, 200 mg, was reduced as described for **1b** under procedure C above. After a reaction time of 30 min, the ether was separated and distilled to a small volume, and the remaining solvent was removed under reduced pressure to yield crystalline material which was triturated with petroleum ether and filtered, 0.15 g, mp 93–120°. After several recrystallizations from alcohol, it melted at 128–130°.

Anal. Calcd for C₁₇H₁₉N₃·½H₂O: C, 74.42; H, 7.34; N, 15.32. Found: C, 74.19; H, 6.84; N, 15.62.

2-Methyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (4f).—The hydrochloride was obtained from a like preparation after the crude crystalline cyano product was converted in the usual manner. The salt weighed 0.112 g (65%) and darkened without melting at 310° (hot stage).

Anal. Calcd for C₁₆H₁₉ClN₂: Cl, 12.90. Found: Cl, 12.64.

The salt was decomposed in aqueous sodium hydroxide–alcohol and the base was recovered with ether. Recrystallized from *n*-hexane–ether it melted at 121–123° (gas). After heating at 80° under reduced pressure for 45 min to remove solvent, it melted at 149–151°; mass spectrum *m/e* 238 (M⁺) 170.

Anal. Calcd for C₁₆H₁₈N₂: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.69; H, 7.73; N, 12.02.

Reductions of 1a. A. In Methanol–Water. 2-(2-Indol-3-ylethyl)-1,2-dihydroisoquinoline (2a).—A solution of 30 mg of sodium borohydride in 0.5 ml of water was mixed with 0.5 ml of methanol and 2.0 ml of ether. To this was added 200 mg of **1a** and the vigorously foaming mixture was stirred until the reaction ended in 3 min with exhaustion of the hydride. The ether layer was separated and 11 mg of **1a** was recovered. After concentration of the ether solution crystallization took place and 98 mg (66%) was recovered from a cold alcohol suspension, vac mp 136–144°. After recrystallization from alcohol it showed vac mp 148–151°; ir spectrum (Nujol) 6.18 (strong), 6.40 μ (medium); nmr spectrum (CDCl₃) ind-NH 7.8 (1 H), ind- α -H 6.9, olefinic CH, AB doublets (*J* = 7.8 Hz) 6.1 (1 H), 5.2 ppm (1 H); and uv spectrum (ethanol) λ_{max} (log ϵ) 334 (3.96), 291 (3.84), 283 (3.83), 276 sh (3.79), 229 (4.15); λ_{min} (log ϵ) 301 (3.70), 287 (3.81), 255 (3.63) [lit.⁴ mp 100° for unpurified product; λ_{max} (log ϵ) 336 (3.83), 293 (3.85), 284 (3.88), 278 sh (3.87), 221 (4.69)].

Anal. Calcd for C₁₉H₁₉N₂: C, 83.18; H, 6.61. Found: C, 83.34; H, 6.37.

2-(2-Indol-3-ylethyl)-1,2,3,4-tetrahydroisoquinoline.—The noncrystalline product from the alcohol wash was converted to a picrate, 40 mg (15%), mp 161–169°. Purified from alcohol it melted at 170–173° [lit.⁴ mp 170–171°]. It was converted to the base with lithium hydroxide and recovered from ether. After recrystallization from alcohol, it melted at 118–120° [lit.⁴ mp 121–122°].

B. In Methanol–Water–Sodium Hydroxide. 2-(2-Indol-3-ylethyl)-1,2-dihydroisoquinoline (2a).—By the procedure detailed for **1b**, 200 mg of **1a** was subjected to reduction in methanolic sodium hydroxide. It was consumed in 2 min. The ether was distilled to a small volume and the residual solvent was removed under reduced pressure. The crystalline residue was filtered from cold alcohol, 129 mg (83%), vac mp 152–154°. A second crop of 10 mg brought the total recovery of **2a** to 89%.

C. In Methanol–Water–Sodium Cyanide. 3-Cyano-2-(2-indol-3-ylethyl)-1,2,3,4-tetrahydroisoquinoline (3a).—A. Sodium borohydride, 30 mg, was dissolved in a solution of 0.2 g of sodium cyanide in 0.3 ml of water. Methanol, 0.5 ml, was added and the solution was layered with 2 ml of ether. **1a**, 200 mg, was

added and the effervescing mixture was stirred. Consumption of the salt was complete in 5 min. The product, 98 mg (63%) mp 137–146°, was recovered from the ether solution in the usual manner. Its identity as **2a** was established by means of an infrared spectrum. The alcoholic filtrate yielded 11 mg (6%) of the crystalline nitrile. B. When the reduction was run in a solution less concentrated in sodium cyanide (0.2 g of sodium cyanide, 0.5 ml of water, 0.5 ml of methanol) the same products were isolated in 50% and 24% yields, respectively. C. To an ice-cold partial solution of 0.2 g of sodium cyanide in 0.3 ml of water was carefully added 0.3 ml of 6 *N* hydrochloric acid. Sodium borohydride, 30 mg, was then dissolved in the still alkaline solution and this was followed by the addition of 0.5 ml of methanol and 2 ml of ether. Reduction of 200 mg of **1a** gave 110 mg (65%) of the nitrile, mp 94–106°. The noncrystalline residue yielded 42 mg (15%) of the picrate of 2-(2-indol-3-ylethyl)-1,2,3,4-tetrahydroisoquinoline. No **2a** could be isolated. D. **2a**, 77 mg, was stirred with a sodium cyanide–hydrogen cyanide solution made as above. The solid became gummy in 30 min and then resolidified on continued trituration. Recovery gave 80 mg (94%), mp 95–105°. Identity with the other nitrile samples was established by its ir (Nujol) spectrum. Recrystallization from alcohol gave a product melting at 108–110°.

Anal. Calcd for C₂₀H₁₉N₃: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.49; H, 6.33; N, 13.70.

The hydrochloride separated as finely divided crystals when the base was added to 3 *N* alcoholic (95%) hydrochloric acid.

Anal. Calcd for C₂₀H₂₀ClN₃: Cl, 10.48. Found: Cl, 10.83.

5,7,8,13,13b,14-Hexahydrobenzo[*g*]indolo[2,3-*a*]quinolizine (4a).—A. The hydrochloride from 60 mg of nitrile **3a** was obtained crystalline in 0.5 ml of 3 *N* alcoholic (95%) hydrochloric acid. The suspension was diluted with an equal volume of water and held on the steam bath for 5 min. The solid became less dense and the vapor was positive to the picrate test for hydrogen cyanide. After washing with alcohol 55 mg (89%) of salt was obtained. B. **2a**, 111 mg, was added portionwise with stirring to 2 ml of 2.4 *N* ethanolic (95%) hydrochloric acid to give a solution which began to deposit crystals in 5 min. Recovery after 1 hr gave 90 mg (71%) of the salt. Identity of material from the two sources was established by ir spectra (Nujol). The salt melted at 290° (lit.¹ mp 287–288°). C. Ether solutions containing mixtures of **2a** and **3a** (from sodium borohydride reductions in cyanide solutions) were extracted with 3 *N* aqueous hydrochloric acid to yield oils which crystallized to give the salt in 60–65% yields.

The base was recovered crystalline from ether–alcohol after decomposing the salt in sodium carbonate solution containing alcohol. It had vac mp 197–200°, air mp 192–195° (lit.¹ mp 188–189°); mass spectrum *m/e* 274 (M⁺) 170.

Registry No.—Sodium borohydride, 16940-66-2; **1c**, 24716-23-2; **1d**, 24716-24-3; **1e**, 24716-25-4; **1f**, 24716-26-5; 1-(2-indol-3-ylethyl)-1,2,5,6-tetrahydropyridine, 24716-27-6; **2a**, 24716-28-7; **3a**, 24716-29-8; **3e**-HCl, 24716-30-1; **3f**, 24716-31-2; **4b** HCl, 24716-32-3; **4c**, 24716-33-4; **4c** HCl, 24716-34-5; **4e**, 24716-35-6; **4e** HCl, 24716-36-7; **4f**, 24716-37-8; **4f** HCl, 24716-38-9.

Biphenylene Insertion Products.

Dibenzoselenophene and Diphenyldibenzostannole

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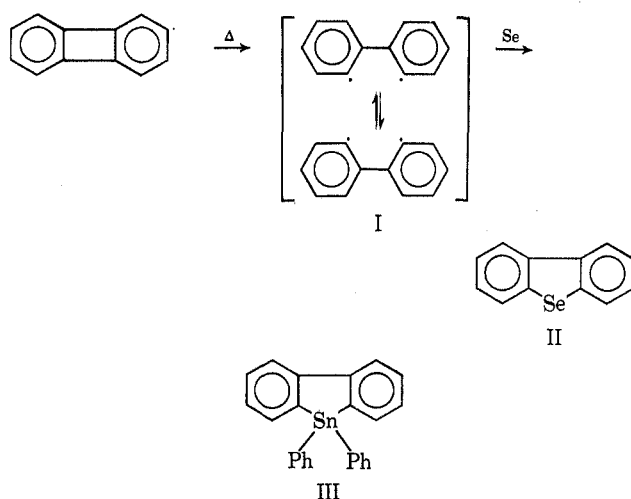
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Received July 15, 1969

A conventional approach to the chemistry of biphenylene, involving synthesis and characterization of ring-substituted derivatives, has revealed a wealth of

detail about this hydrocarbon.¹⁻³ Until recently, a chemistry directly involving the central ring was thought not to exist.⁴ The unique feature of this hydrocarbon, its strained four-membered ring, is only now receiving a full measure of attention.⁴⁻⁸

Some observations we made are especially germane to the chemistry of the inner ring. If selenium and biphenylene are refluxed together at *ca.* 275° for 22 hr, dibenzoselenophene (II) is formed (14% based on starting materials; *ca.* 75% recovery of biphenylene). Reaction for longer times leads to extensive tarring and decreased yields of dibenzoselenophene (II), apparently by its further reaction with the ring-opened diradical I.

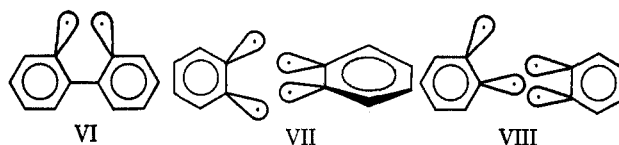


Reaction of $(\text{Ph}_2\text{Sn})_6$ ⁹ with biphenylene led to several new products in low yield. The quantity of material available did not permit isolation of the separate products, but thin layer chromatography showed a product with the same R_f value as authentic diphenyldibenzostannole (III)^{9,10} upon elution with each of 13 different solvents. The mass spectrum of the product showed peaks attributable to III. This material is not present in the pyrolysis products of $(\text{Ph}_2\text{Sn})_5$ or Ph_4Sn . Owing to lack of starting materials, optimum conditions for this reaction were not determined.

Biphenylene gave no insertion products upon pyrolysis with Te,¹¹ Ph_3P ,¹² or SO_2 (1 atm), and most of the biphenylene was recovered. Insertion of SO_2 would have provided a route to dibenzothiophenes from biphenylenes (the direct route from elemental sulfur is closed; only black tar is obtained⁴).

Representation of the reactive intermediate as I is not intended to distinguish between VI, VII, and VIII.

Unlike VI, the species represented by VII and VIII both allow a 1,8-disubstituted biphenylene to yield a 1,5-disubstituted dibenzoselenophene. Likewise, quenching VII or VIII could give a rearranged bi-



phenylene. The observed fragmentation of I to produce benzyne⁴ argues for the intervention of VII or VIII if only as higher energy intermediates.

Experimental Section

The boiling point of biphenylene was determined to be 275 ± 5° by capillary microtechnique. Specified quantities of reagents in ordinary nmr tubes were heated at this temperature for the indicated times in an electrically heated aluminum block (Gallenkamp melting point apparatus).

Dibenzoselenophene (II).—Biphenylene (0.001 mol, 0.152 g) and selenium powder (0.200 g, 2.5-fold excess) were refluxed for 22 hr. The reaction mass was extracted with THF (0.148 g recovered, mp 105–110°) and examined by vpc, tlc, and nmr. Retention time, R_f values (ligroin, benzene), and nmr spectrum^{13,14} were identical with those of authentic dibenzoselenophene. The product identification was confirmed by melting point and mixture melting point. The yield was 14% based on starting materials, and 75% biphenylene was recovered.

When a similar reaction was allowed to proceed for 65 hr, considerable darkening was noted, and THF extraction yielded only 60 mg of material. The relative amount of dibenzoselenophene was now only 5% of the biphenylene present (integration by nmr), and tlc showed the presence of four slower moving spots. Even when the reaction was allowed to proceed for only 40 hr, extensive tarring occurred.

9,9-Diphenyldibenzostannole (III).—Diphenylstannene pentamer (0.001 mol, 0.273 g) and biphenylene (0.001 mol, 0.153 g) were refluxed for 42 hr. The material soluble in THF was extracted and dried (0.250 g). Tlc and nmr showed the presence of unreacted biphenylene (0.105 g by comparison with an added reference). The extracted product was spotted on Eastman chromatogram SiO_2 tlc sheets and developed with each of the 13 solvents (see Table I).

Vpc spectra likewise indicated the presence of III. On SE-30 (3 ft × 1/8 in., 250°), the THF extract showed a small peak (*ca.* 0.5% of total) with the retention time (20 min) of the diphenyldibenzostannole, along with seven others, and on QF-1 (12 ft × 0.25 in., 250°), the stannole peak (17 min) and six others were observed. There was only one other peak (which was of roughly equal size) within 5 min of the stannole peak on either column. Diphenyldibenzostannole was not eluted from a carbowax column (12 ft × 0.25 in., 250°) after 45 min.

The mass spectrum of the product showed relatively strong peaks at the positions and with the isotopic distribution expected for (III minus H)⁺ and (III minus phenyl)⁺; other peaks indicated the presence of Ph_3Sn_2^+ and higher molecular weight diphenyltin polymers.

Attempted Insertion of Triphenylphosphine.—Biphenylene (0.001 mol, 0.152 g) and triphenylphosphine (0.002 mol, 0.542 g) were refluxed for 30 hr. At the end of that time, biphenylene (0.13 g) was removed by sublimation, and the remaining product showed only Ph_3P and a trace of Ph_3PO (identified by mixture melting point and mass spectrometry).






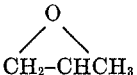
Attempted Insertion of Tellurium.—Biphenylene (0.001 mol, 0.152 g) and tellurium (0.0023 mol, 0.284 g) were refluxed for 28 hr. The reaction mass was extracted with THF, yielding 0.276 g of Te (insoluble) and 0.140 g of soluble product (biphenylene, mp 108–110°). No new compounds could be detected in the recovered biphenylene by tlc or nmr.

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TABLE I

Solvent	R_f , product	R_f , III	Resolution
	0.16, 0.34	0.16	Good
	0.13, 0.40	0.13	Good
Ligroin (bp 60–80°)	0.07, 0.15, 0.21, 0.26, 0.41	0.15	Good
CCl ₄	0.21, 0.25, 0.31, 0.44, 0.59	0.44	Good
CCl ₂ F–CClF ₂ (Freon 113)	0.20, 0.51	0.20	Good
	0.62–0.79	0.68	Partial
	0.53–0.70	0.58	Partial
	0.45–0.69	0.56	Partial
CHCl ₃	0.70	0.70	Poor
(CH ₂ Cl) ₂	0.58–0.68	0.65	Poor
CH ₃ CCl ₃	0.64	0.64	Poor
C ₆ H ₆	0.57–0.68	0.59	Poor
	0.62–0.78	0.65	Poor

Attempted Insertion of SO₂.—Biphenylene (0.001 mol, 0.151 g) was refluxed under a slow stream of SO₂ for 41 hr. There was a slight gain in weight (0.001 g vs. the theoretical 0.064 g), and the reaction product upon thin layer chromatography showed two new products in very low yield, but neither was the desired sulfone, and the products were not characterized.

Registry No.—Biphenylene, 259-79-0; II, 244-95-1; III, 5381-63-5.

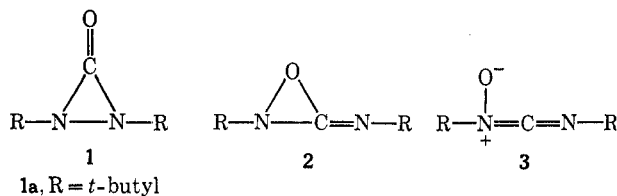
Diaziridinones. V.^{1a} Reduction by Phosphite to Carbodiimide and Peracid Oxidation of Carbodiimide to Diaziridinone^{1b}

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Received August 28, 1969

Previous papers have described the synthesis and some reactions of diaziridinones (1).^{1a,2} Consideration of possible valence isomers 2 and 3 of 1 led to a synthesis of 1 by reaction of RNO with RNC.^{1a} We consider here the possibility of preparation of 1 *via*

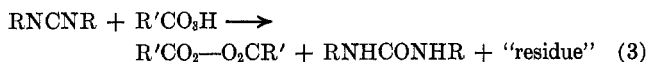
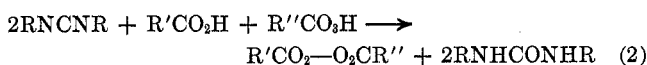
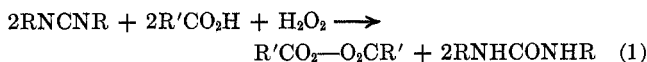


(1) (a) Part IV: F. D. Greene and J. F. Pazos, *J. Org. Chem.*, **34**, 2269 (1969). (b) Financial support from the National Science Foundation (Grant No. GP-5527) is gratefully acknowledged.

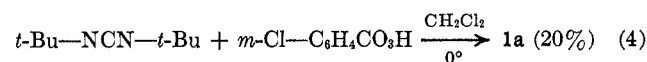
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2 or 3 by the oxidation of a carbodiimide and the reverse problem of removal of oxygen from a diaziridinone, with conversion to a carbodiimide.

Peracid Oxidation of Carbodiimide.—Reaction of dicyclohexylcarbodiimide with carboxylic acids and hydrogen peroxide (eq 1) or with a carboxylic acid and a percarboxylic acid (eq 2) affords diacyl peroxides in good yield.³ Reaction of dicyclohexylcarbodiimide with a peracid afforded the urea and diacyl peroxide in moderate yield along with a residue which could not be characterized (eq 3).³



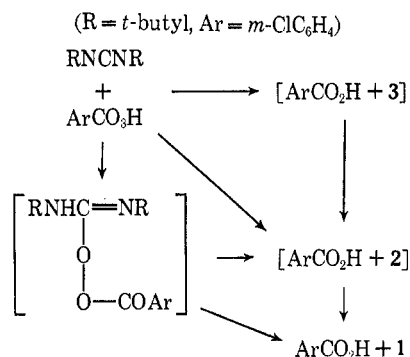
Use of a more hindered carbodiimide, di-*t*-butylcarbodiimide, and *m*-chloroperbenzoic acid in methylene chloride has resulted in the isolation of di-*t*-butyldiaziridinone (1a) in 20% yield. The yield of 1a was ap-



proximately the same when the reaction was carried out in a vigorously stirred two-phase system of methylene chloride and a phosphate buffer. When the reaction was carried out in carbon tetrachloride and monitored continuously by ir, diaziridinone bands (1880 cm⁻¹) built up immediately.

The major possibilities for diaziridinone formation are summarized in Scheme I. The generation of car-

SCHEME I



boxylic acid in the reactions of Scheme I and the greater reactivity of RCO₂H in comparison with RCO₃H toward carbodiimide³ provide additional paths for reaction accounting for the complexities in eq 3 (R = cyclohexyl) and for the low yield of 1a in eq 4.

Phosphite Reduction of Diaziridinone.—The possibility of formation of 1 *via* 2 or 3, indicated above and in the reaction of RNO with RNC,^{1a} raises the question of the reversible formation of 2 or 3 from 1. Phenyl isocyanate, a species which appears to trap an inter-

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