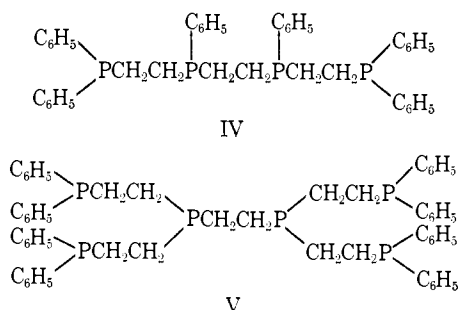
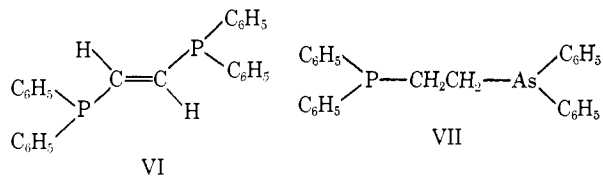


isomeric to III is $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (IV),³ mp 155–158°, which may be prepared in 56% yield from $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ ⁴ and $(C_6H_5)_2PCH=CH_2$ in boiling benzene for 24 hr in the presence of a potassium *t*-butoxide catalyst. Further extension of this new synthesis results in the preparation of the potentially hexadentate ligand $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (V), mp 138–140°, in ~20% yield from $H_2PCH_2CH_2PH_2$ ⁵ and excess $(C_6H_5)_2PCH=CH_2$; the hexatertiary phosphine V is the first known potentially hexadentate tertiary phosphine ligand.⁶



In an attempt to explore the possible utility of the new synthetic method for preparing phosphines with $-CH=CH-$ bridges, the reaction between $(C_6H_5)_2PH$ and $(C_6H_5)_2PC\equiv CH$ ⁷ was investigated (boiling benzene, 14 hr, phenyllithium catalyst). A 66% yield of *trans*- $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ (VI)⁸ was obtained; identification of this material as the *trans* isomer was based on its infrared and nmr spectra⁸ and upon its reaction with $CH_3Mo(CO)_3C_5H_5$ to give a $(diphos)[Mo(CO)_2(CO-CH_3)C_5H_5]_2$ rather than a $(diphos)_2Mo(CO)_2$ derivative.⁹ This result suggests that base-catalyzed addition of the phosphorus-hydrogen bond across the carbon-carbon triple bond of an ethynylphosphine is stereospecific resulting in the *trans* isomer. Unfortunately unsaturated tertiary phosphines such as VI cannot act as chelating agents because of the unfavorable relative locations of the phosphorus atoms.¹⁰



Another extension of this new synthetic technique enables the preparation of unusual "mixed" tertiary phosphine-arsines by addition of diphenylarsine to a vinylphosphine or ethynylphosphine using a potassium *t*-butoxide catalyst¹¹ in boiling benzene. Thus the reaction of $(C_6H_5)_2AsH$ with $(C_6H_5)_2PCH=CH_2$ gives

(4) (a) K. Issleib and H. Weichmann, *Ber.*, 101, 2197 (1968). (b) The starting material $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ can also be prepared in ~21% yield by cleavage of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with sodium metal in liquid ammonia.

(5) L. Maier, *Helv. Chim. Acta*, 49, 842 (1966).

(6) For a report of a hexadentate polytertiary arsine ligand, see C. M. Harris and J. V. Kingston, *Chem. Commun.*, 965 (1968).

(7) C. Charrier, M. P. Simonnin, W. Chodkiewicz, and P. Cadot, *Compt. Rend.*, 258, 1537 (1964).

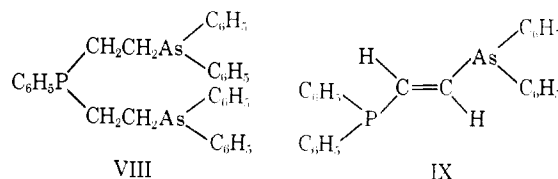
(8) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, 86, 2299 (1964).

(9) R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, 8, 1792 (1969).

(10) R. B. King and A. Efraty, *ibid.*, in press.

(11) Phenyllithium could not be used as a catalyst for reactions of $(C_6H_5)_2AsH$.

a 65% yield of 1-diphenylphosphino-2-diphenylarsinoethane, $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ (VII),³ mp 116–118°. Similarly the reaction of $(C_6H_5)_2AsH$ with $C_6H_5P(CH=CH_2)_2$ gave a 62% yield of $C_6H_5P[CH_2CH_2As(C_6H_5)_2]_2$ (VIII),³ mp 160–162°. Reaction of $(C_6H_5)_2AsH$ with $(C_6H_5)_2PC\equiv CH$ gives a 66% yield of *trans*- $(C_6H_5)_2PCH=CHAs(C_6H_5)_2$ (IX),³ mp 95–96°. The proton nmr spectrum of IX besides exhibiting a strong phenyl resonance at τ 2.7–2.8 exhibits two overlapping doublets at τ 3.07 ($J = 14.5$ cps) and τ 3.10 ($J = 16$ cps) indicating a slight chemical shift difference between the two vinyl protons arising from the fact that one is bonded to a carbon bonded to phosphorus and the other is bonded to a carbon bonded to arsenic.



An investigation of the complexes formed by these polytertiary phosphines and arsines upon reaction with metal carbonyl and metal halide derivatives is currently in progress.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-68-1435 and to the University of Georgia Office of General Research for the support of P. N. K. during the course of this work. We also thank Dr. R. C. Taylor for providing samples of $C_6H_5PH_2$ and $H_2PCH_2CH_2PH_2$.

(12) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(13) Postdoctoral Research Associate.

R. B. King,¹² Pramesh N. Kapoor¹³
Department of Chemistry, University of Georgia
Athens, Georgia 30601

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The Stability of Isoindoles

Sir:

Interest both in the synthesis¹ and the stability^{1a,2} of isoindoles has grown considerably in recent years. Yet in spite of the resurgence of synthetic activity and the long history of this class of compounds³ it was only a short time ago that the first isolable N-unsubstituted isoindoles were reported,^{1a,c} all of these compounds bore one or more aryl groups in the pyrrole ring. Indeed, it is a striking fact that there is no example to date in the literature of an isolable isoindole in which the pyrrole moiety is free of substituents. To be sure, the parent compound, isoindole,^{1b} and its relative, benz[*f*]isoindole,^{1d} have been prepared recently, but they are known only in solution. This situation has raised the

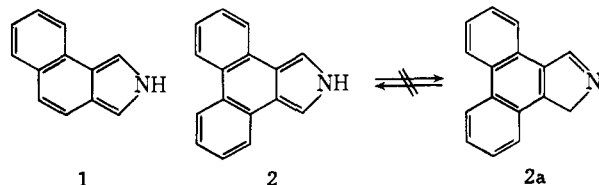
(1) For examples: (a) D. F. Veber and W. Lwowski, *J. Amer. Chem. Soc.*, 86, 4152 (1964); (b) R. Kreher and J. Seubert, *Z. Naturforsch.*, 20b, 75 (1965); (c) J. C. Emmett and W. Lwowski, *Tetrahedron*, 22, 1011 (1966); (d) J. Shields and J. Bornstein, *Chem. Ind. (London)*, 1404 (1967); (e) C. O. Bender and R. Bonnett, *J. Chem. Soc.*, 3036 (1968); (f) M. E. Mann and J. D. White, *Chem. Commun.*, 420 (1969).

(2) (a) J. Kopecky, J. E. Shields, and J. Bornstein, *Tetrahedron Lett.*, 3669 (1967), and references cited therein; (b) R. C. Anderson and R. H. Fleming, *ibid.*, 1581 (1969).

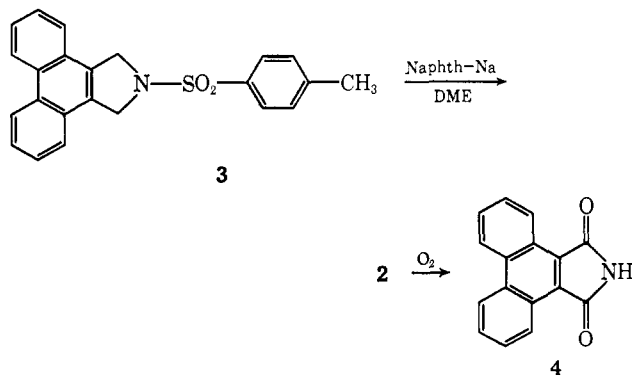
(3) R. C. Elderfield and T. N. Dodd, Jr., in "Heterocyclic Compounds," Vol. III, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1952, p 275 ff.

question whether isoindoles devoid of substituents in the pyrrole ring would be sufficiently stable to permit isolation.

Recent HMO calculations^{2a} have led us to predict that the hypothetical compounds benz[*e*]isoindole (**1**) and dibenz[*e,g*]isoindole (**2**) should possess a sufficiently high degree of stability to yield to isolation. To test the validity of our predictions we decided to attempt the synthesis of structure **2** at this time since the starting compounds were readily accessible. We now wish to report the synthesis and isolation of **2**, the first example of a stable isoindole totally unsubstituted in the pyrrole ring.



The synthetic route to dibenz[*e,g*]isoindole (**2**) involved the base-induced elimination of *p*-toluenesulfonic acid from 2-(*p*-toluenesulfonyl)dibenz[*e,g*]isoindoline (**3**). This method, which has worked well in the preparation of isoindole^{1b} and its derivatives,^{1d} afforded only traces of **2** when the usual bases, potassium *t*-butoxide or phenyllithium, were used. Subsequently, sodium naphthalene radical anion⁴ was found to be especially effective in the synthesis of **2**. The desired sulfonamide **3**, mp 275–276° dec (from dimethylformamide), was obtained in 80% yield by dialkylation of *p*-toluenesulfonamide⁵ with 9,10-bis(bromomethyl)phenanthrene.⁶ *Anal.* Calcd for C₂₃H₁₉NO₂S: C, 73.97; H, 5.13; N, 3.75; S, 8.59. Found: C, 73.97; H, 5.24; N, 3.61; S, 8.42. Treatment of **3** with 5 equiv of 0.75 *M* sodium naphthalene in dimethoxyethane for 1 hr in a nitrogen atmosphere afforded, after hydrolysis, a mixture of naphthalene and isoindole **2**. Naphthalene was easily removed by sublimation [50° (10 mm)]; the remaining crude solid was readily purified by sublimation [150° (1 mm)] or by recrystallization from benzene–hexane to give **2** as colorless needles, mp 161–162° (71%). *Anal.* Calcd for C₁₆H₁₁N: C, 88.45; H, 5.10; N, 6.48; mol wt, 217. Found: C, 88.24; H, 4.97; N, 6.68; mol wt, 211 (osmometry).



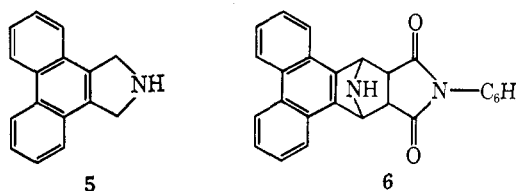
(4) Although this reagent has been reported by W. D. Closson and his coworkers (*J. Amer. Chem. Soc.*, **89**, 5311 (1967)) to effect the reductive cleavage of sulfonamides, we observed no dibenz[*e,g*]isoindoline (**5**) formation.

(5) For a general method see J. Bornstein and J. E. Shields, *Org. Syn.*, **47**, 110 (1967).

(6) S. Hauptmann, *Chem. Ber.*, **93**, 2604 (1960).

Dibenz[*e,g*]isoindole has $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ) 210 (22,000), 230 (24,100), 250 (25,700), 260 (26,000), 276 (17,300), 288 (11,500), 301 (11,000), 314 (10,400), 352 (1780), and 385 (880). The ir spectrum (CHCl₃) shows a sharp peak for NH at 3460 cm⁻¹; the nmr spectrum (CDCl₃) reveals aromatic protons centered at τ 2.12 and a broad NH signal at τ 1.20 (exchanges with D₂O in neutral solution). The absence of the tautomeric isoindolenine **2a** is indicated by the lack of benzylic proton absorption. Compound **2** is remarkably stable both in the solid state and in deoxygenated solutions. However, in the presence of oxygen, solutions of **2** undergo light-catalyzed conversion to phenanthrene-9,10-dicarboxyimide (**4**).⁷ In a typical experiment, an oxygen-saturated solution of **2** in benzene was irradiated (2537 Å) for 4 hr. The crude precipitate was chromatographed on a column of silica gel with benzene as eluent to give, after recrystallization from xylene, 60% of imide **4**.⁸ In contrast to our findings, the *N*-substituted isoindoles 1,2,3-triphenylisoindole and 1,3-diphenyl-2-methylisoindole have been reported to undergo oxidative hydrolysis⁹ to *o*-dibenzoylbenzene. We observed no extrusion of nitrogen when **2** was oxidized in the presence of water.

Reduction of **2** with coppered zinc dust in refluxing acetic acid required 48 hr. Purification of the reaction product by sublimation [150° (1 mm)] followed by recrystallization from benzene–hexane afforded dibenz[*e,g*]isoindoline (**5**, 65% yield) as colorless needles, mp 156–157° dec. *Anal.* Calcd for C₁₆H₁₃N: C, 87.64; H, 5.97; N, 6.38. Found: C, 87.38; H, 6.10, N, 5.99. The ir spectrum (Nujol) shows NH at 3350 cm⁻¹; the uv spectrum has $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ) 210 (43,000), 222 (30,900), 248 (60,000), 255 (70,900), 270 (11,200), 277 (10,000), 288 (9000), 300 (9500), 321 (840), 327 (730), 336 (810), 344 (625), and 353 (810), compatible with the spectrum of 9,10-dimethylphenanthrene.⁷ The nmr spectrum (DMSO-*d*₆) consists of a multiplet of eight aromatic protons at τ 1.82, NH at 3.00, and four benzylic protons as a singlet at 5.44. Treatment of **5** with *p*-toluenesulfonyl chloride in pyridine afforded the original sulfonamide **3**.



Unlike the previously reported less-stable isoindoles,¹ dibenz[*e,g*]isoindole does not react readily with dienophiles. An oxygen-free benzene solution of **2** and *N*-phenylmaleimide afforded, after standing 3 weeks, adduct **6** (45%) as felted needles,¹⁰ mp 156–157° dec. The nmr spectrum of **6** could not be obtained since the adduct, like those of certain other isoindoles,^{1a,d} dissociates in concentrated solution to give a spectrum indicative of the presence of a mixture of **2** and *N*-phenylmaleimide. This tendency of **6** to revert to

(7) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5544 (1964).

(8) Identified by comparison with an authentic sample, kindly furnished by Professor Timmons.

(9) W. Theilacker and W. Schmidt, *Ann.*, **605**, 43 (1957).

(10) Elemental analysis indicated a 1:1 adduct containing 1 mol of benzene. Attempts to remove the solvent by heating *in vacuo* led to dissociation of the adduct.

its progenitors was further confirmed by thin layer chromatography and by the appearance of a blue color with Ehrlich's reagent within a few minutes of dissolution of the adduct.¹¹ It was possible to obtain uv and ir data for **6** and these support the Diels-Alder structure.

(11) In contrast, isoindole **2** reacts at once with Ehrlich's reagent. (Compound **2** also gives an immediate deep violet color in the pine splint test.)

Joan E. Shields

Department of Chemistry, C. W. Post College
Brookville, New York 11548

Joseph Bornstein

Department of Chemistry, Boston College
Chestnut Hill, Massachusetts 02167

Received June 20, 1969

The Catalytic Fixation of Molecular Nitrogen by Electrolytic and Chemical Reduction

Sir:

For some years this laboratory has been investigating the chemical modification of molecular nitrogen under mild conditions, by means of experiments based on the concept of titanium(II) as the fixing species.¹⁻⁵ We now wish to report the innovation of an electrochemical system in which titanium *catalytically* effects reduction of nitrogen to the ammonia level.

In the most successful experimental variation,⁶ the electrolysis cell was fitted with an aluminum anode and a nichrome cathode, and contained a 60-ml 1,2-dimethoxyethane (glyme) solution of 1.68 mmol of titanium tetrakispropoxide, 7.6 mmol of naphthalene, 8.6 mmol of tetrabutylammonium chloride, and 42 mmol of aluminum isopropoxide. The solution, while being stirred under a slow stream of pure nitrogen, was electrolyzed at 40 V until the conductance of the cell had greatly diminished (11 days); during this time 0.155 faradays had passed through the cell and 15.1 mmol of aluminum had been lost from the anode. When the solution was treated with 40 ml of 8 M aqueous sodium hydroxide solution and heated in a water bath, the product ammonia (10.2 mmol, 610% yield, based on $\text{NH}_3:\text{Ti}$ molar ratio) could be blown into an aqueous hydrochloric acid trap by a stream of gas.

When titanium tetrakispropoxide was omitted or when argon was substituted for nitrogen, no ammonia could be detected. In the absence of naphthalene, ammonia was formed, but in decreased yield. Apparently, the naphthalene functions primarily as an electron carrier, being reduced to naphthalide by the cathode and oxidized back to naphthalene by titanium-nitrogen species. Indications of the presence of naphthalide are: (1) attack of the Teflon-coated stirring bar (a property of sodium naphthalide and some other strong reducing agents) only when naphthalene is included, and (2) when the titanium tetrakispropoxide is

(1) E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.*, **87**, 3277 (1965).

(2) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *ibid.*, **89**, 5707 (1967).

(3) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(4) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(5) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *ibid.*, **91**, 1551 (1969).

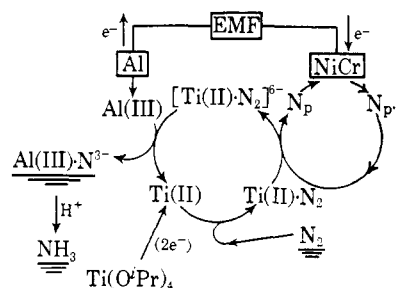
(6) Yields varied between 257 and 610%.

omitted, generation of a dark greenish brown substance (sodium naphthalide in glyme is an intense brownish green) at the cathode.⁷ It should be noted that naphthalide does not react with aluminum isopropoxide in glyme, as determined in a separate series of experiments.

We conjecture that the aluminum isopropoxide, in addition to serving as an electrolyte, frees the lower valent titanium compound of reduced nitrogen so that it can fix more molecular nitrogen.⁸ In keeping with this hypothesis is the observation that, in a single cycle, the chemical fixation-reduction of nitrogen becomes catalytic with respect to titanium (275% NH_3) when aluminum isopropoxide is included in the previously reported^{2,3} reaction of sodium metal with a glyme solution of naphthalene and titanium tetrakispropoxide.

Our observations to date are consistent with the reaction sequences diagrammed in Chart I. The elec-

Chart I^a



^a Lower valent titanium may be monomeric or polymeric.

trolytic reduction of nitrogen and aspects of related titanium-aluminum systems are under continuing investigation at this time.

Acknowledgment. Financial support was provided by the National Institutes of Health (Grant GM 13797).

(7) Apparently the naphthalide is oxidized by tetrabutylammonium ion in the absence of titanium tetrakispropoxide and not by the anode since the dissolution of aluminum accounts for 99% of the electrons recovered from the anode. Tributylamine can be recovered from the reaction mixture after work-up (82%). However, it is clear that the tetrabutylammonium chloride is being slowly consumed in some way, since the conductivity of an electrolysis solution after prolonged electrolysis is a fraction of its initial value and can be restored by addition of more tetrabutylammonium chloride. When sodium naphthalide is allowed to react with tetrabutylammonium chloride under a stream of nitrogen, tributylamine is found in the reaction flask and 1,2-dibromobutane is found in a dilute bromine solution through which the effluent gas is passed.

(8) Cf. M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Commun.*, 1074 (1968).

(9) National Institutes of Health Postdoctoral Fellow, 1969-.

Eugene E. van Tamelen, Douglas A. Seeley⁹

Department of Chemistry, Stanford University
Stanford, California 94305

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Photochemistry without Light

Sir:

We wish to report a general method for achieving "photochemistry without light."¹ The principle in-

(1) This expression has been used previously in a specific case where it was suggested that a common intermediate might have been involved in a photochemical and a nonphotochemical reaction: H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).