To a solution of 1 g. of 2,3-diphenyl-1,4-naphthoquinone in 30 ml. of glacial acetic acid, 1 g. of powdered zinc and 5 ml. of concentrated hydrochloric acid were added. The mixture was boiled until the solution became colorless (5–10 min.) and a white solid separated. The mixture was then cooled, diluted with 200 ml. water, and extracted with methylene chloride. To the dried extract there were added immediately 1 ml. of pyridine and 1 ml. of acetyl chloride with cooling. The pale yellow solution was evaporated to dryness, and the residue was triturated with ethanol. The white crystals of **2,3-diphenylnaphthalene-1,4-diol diacetate** were collected and recrystallized from ethanol to yield 350 mg. of product, m.p. 199–200°, unchanged by further crystallization; lit.[10] m.p. 200–202°; ultraviolet spectrum: λ_{max}^{EtOH} 219 (ϵ 45,600) and 232 mμ (45,000).

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.69; H, 5.06.

2,3-Epoxy-2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone.—To a hot solution of 1 g. (3.2 mmoles) of 2,3-diphenyl-1,4-naphthoquinone in 25 ml. of ethanol there were added 3 ml. of 30% hydrogen peroxide and 5 ml. of 10% aqueous sodium carbonate. The solution turned deep red and then colorless. After heating for 5 min., a solid separated. The mixture was cooled, diluted with 100 ml. of water and filtered. Two recrystallizations of the precipitate from ethanol yielded 720 mg. (2.2 mmoles, 69%) of **2,3-epoxy-2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone**, m.p. 159–160°; lit.[11] m.p. 155–166°; ultraviolet spectrum: λ_{max}^{EtOH} 235 mμ (ϵ_{max} 37,200).

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 81.08; H, 4.35.

Reductive Cleavage of II with the Dianion of 2,3-Diphenylnaphthalene-1,4-diol.—A solution of 1.0 g. (3.2 mmoles) of 2,3-diphenyl-1,4-naphthoquinone (III) in 50 ml. of dioxane was hydrogenated for 30 min. at 50 lb./in.[2] using 0.5 g. of platinum oxide as catalyst. After removal of the catalyst the solution was added to a suspension of 300 mg. (6.4 mmoles) of sodium hydride (51.6% in mineral oil) in 50 ml. of dioxane with stirring under nitrogen. After the evolution of gas ceased, a light brown-yellow solution was obtained. To this solution there was added with stirring a solution of 1.414 g. (3.2 mmoles) of II in 50 ml. of dioxane. The red solution was stirred at room temperature overnight and concentrated to a thick sirup. This was diluted with methylene chloride and extracted once with 0.1 *N* sodium hydroxide and once with water. The yellow organic phase was concentrated to a gum, which on trituration with methanol gave 1.88 g. of a yellow solid containing 0.87 g. (1.95 mmoles, 61%) of unchanged II and 1.0 g. (100%) of **2,3-diphenyl-1,4-naphthoquinone**. The concentrations of these two substances in the mixture were determined by ultraviolet spectroscopy from the optical density at 231 mμ of a solution in ethanol.

The red aqueous phase after acidification and extraction with methylene chloride gave 0.41 g. (1.84 mmoles, 29%) of **2-phenyl-1,3-indandione**.[17]

The Photochemical Conversion of Phenyl Isocyanate and Diphenyldiazomethane to 2,2-Diphenylindoxyl

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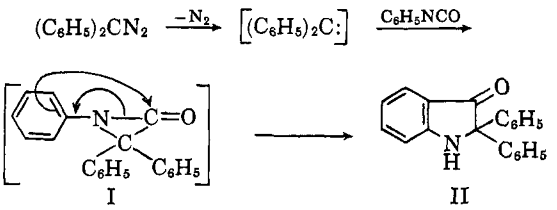
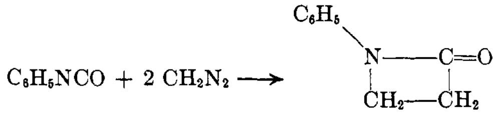
We have found that phenyl isocyanate and diphenyldiazomethane react under the influence of ultraviolet light to afford 2,2-diphenylindoxyl.[1] This reaction appears to be the first example of the addition of a carbene to an isocyanate and the first photoinitiated reaction of an isocyanate. In addition, each reactant is converted individually into a characteristic irradiation product; that is, diphenyldiazomethane produces benzophone azine[2] and phenyl isocyanate gives the cyclic dimer 1,3-diphenyluretedione.[3]

The formation of 2,2-diphenylindoxyl can be explained by assuming that the photo-generated carbene from diphenyldiazomethane adds to the phenyl isocyanate to produce an α-lactam I which then collapses to the indoxyl II.



Recently[1] this same α-lactam I was proposed as an intermediate in the reaction of α-chloro-α,α′-diphenylacetanilide with sodium hydride; in that case also 2,2-diphenylindoxyl (II) was the principal product.

In two earlier communications from this laboratory[4,5] the nonphotochemical reaction of diazomethane with phenyl isocyanate was reported to give a β-lactam (that of N-phenyl-β-alanine). At that time it was suggested[5] as one possible mechanism that first one molecule of diazomethane reacted with one molecule of phenyl isocyanate to give an intermediate α-lactam, which on subsequent reaction with a second molecule of diazomethane formed the β-lactam.



Staudinger stated[6] that diphenyldiazomethane does not react with phenyl isocyanate. Our present experiments confirm the absence of a detectable change on simple mixing of the reagents; heating decomposes diphenyldiazomethane to benzophenone azine. Irradiation, however, initiates a rapid reaction.

Experimental

Irradiation of Phenyl Isocyanate and Diphenyldiazomethane.—A solution of diphenyldiazomethane (1.2 g., 6.2 mmoles) in phenyl isocyanate (3.5 g., 29.6 mmoles) was irradiated[7] in a quartz tube with occasional cooling. After 6 hr. 115 ml. of nitrogen (25°) had been evolved and the deep violet color of diphenyldiazomethane had disappeared. The excess phenyl isocyanate was evaporated at room temperature and the residue was chromatographed over silicic acid (Mallinckrodt, 100 mesh). Elution with *n*-pentane–benzene yielded **benzophenone azine** (356 mg., m.p. 162–163°). Benzene eluted **1,3-diphenyluretedione** (53 mg., m.p. 174–175°); both were characterized by comparison with samples prepared by known methods.[2,3] Elution with benzene–ether (97:3) afforded 312 mg., m.p. 212–213° (after recrystallization from ether–petroleum ether), of **2,2-diphenylindoxyl**. Identification was made by mixture melting point and comparison of infrared and ultraviolet spectra with an authentic sample.[1] The molecular weight (mass spectrometric) was 285 (calcd. for $C_{20}H_{15}NO$: 285). Continued elution with benzene–ether gave a viscous red oil in which the probable pres-

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(1) J. C. Sheehan and J. W. Frankenfeld, *J. Am. Chem. Soc.*, **83**, 4792 (1961).

(2) T. Curtius and F. Rauterberg, *J. prakt. Chem.*, [2] **44**, 200 (1891).

(3) L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, **8**, 230 (1943).

(4) J. C. Sheehan and P. T. Izzo, *J. Am. Chem. Soc.*, **70**, 1985 (1948).

(5) J. C. Sheehan and P. T. Izzo, *ibid.*, **71**, 4059 (1949).

(6) H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, **49**, 1928 (1916).

(7) The irradiation was carried out from a distance of 12–15 cm. with a 140-w. Hanovia Utility Model high-pressure quartz mercury-vapor arc lamp, which transmits the complete ultraviolet spectrum.

ence of 1,3-diphenyloxindole[1] was detected by thin layer chromatography (silica gel G and aluminum oxide G in four different solvent systems: 97% benzene–3% ether, 99% benzene–1% ethyl acetate, 99% benzene–1% dioxane, and 99% benzene–1% methanol).

However, two other products,[1] which are derivable from the α-lactam I, namely 1-keto-2,3-diphenylisoindole and 3,3-diphenyloxindole, could not be found.

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The Synthesis of Naphtho[2,1-*a*]perylene and Dibenzo[*ae*]perylene[1,2]

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Many papers attest to the fact that a causal relationship very likely exists between air pollution and respiratory diseases including lung cancer.[6] A relationship between polynuclear aromatic hydrocarbons found in certain polluted air and lung cancer is also suggested.[7] Continuing our work in this area,[8] we were concerned with the dehydrogenation of 7-(1-naphthyl)benz[*a*]anthracene (I). This compound, on catalytic intramolecular dehydrogenation, might lead to dibenzo[*ae*]perylene (II) and/or naphtho[2,1-*a*]perylene (III). When I was dehydrogenated with aluminum chloride and stannic chloride, only one perylene derivative was found. In order to establish the structure of the product, which was either II or III, we undertook an unequivocal synthesis of naphtho[2,1-*a*]perylene (III).

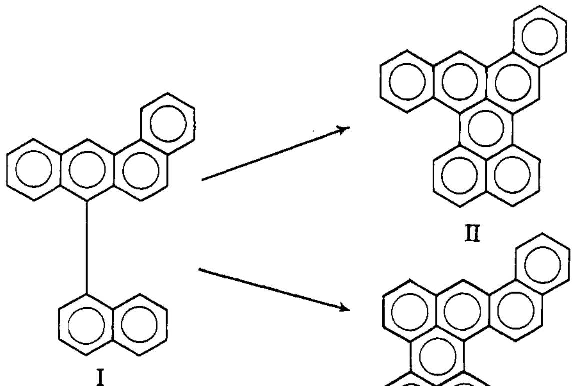
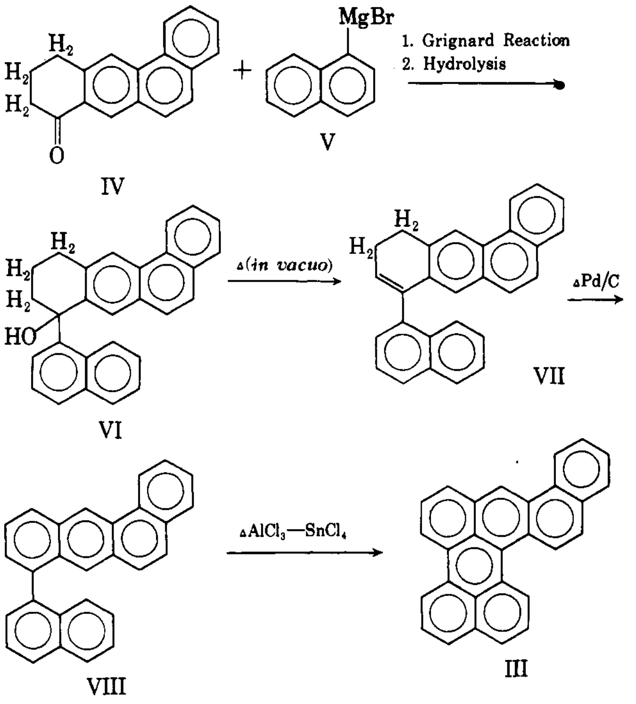


Chart I



On the basis of similar experiments,[9] it seemed that if we could prepare 8-(1-naphthyl)benz[*a*]anthracene (VIII), an unequivocal dehydrogenation to III might be achieved. The reactions shown in Chart I were undertaken to this end. A four-step reaction sequence was used to prepare 8-keto-8,9,10,11-tetrahydrobenz[*a*]anthracene (IV).[10] The action of 1-naphthylmagnesium bromide on this ketone followed by hydrolysis afforded a mixture of 8-(1-naphthyl)-8-hydroxy-8,9,10,-11-tetrahydrobenz[*a*]anthracene (VI) in a 22% yield and the dehydrated product, 8-(1-naphthyl)-10,11-dihydrobenz[*a*]anthracene (VII) in 13% yield. Satisfactory analytical data could not be obtained on the carbinol VI due to its easy dehydration on crystallization. The carbinol was converted quantitatively to the dehydration product 8-(1-naphthyl)-10,11-dihydrobenz[*a*]anthracene (VII) when it was heated *in vacuo*. VII on dehydrogenation with a palladium-on-charcoal catalyst in boiling *p*-cymene gave 8-(1-naphthyl)benz[*a*]anthracene (VIII) in 83% yield.

Many known dehydrogenation agents and reaction procedures[8] were used in an attempt to convert VIII to naphtho[2,1-*a*]perylene (III); heating with sulfur, with selenium, with palladium on carbon; vapor phase dehydrogenation at 430° on asbestos; fusion with sodium chloride and aluminum chloride[11]; pyrolysis at 700°; aluminum chloride in boiling benzene[8];

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[1] The nomenclature used in this paper is that presented in the "Definitive Rules for Nomenclature of Organic Chemistry," *J. Am. Chem. Soc.*, **82**, 5545 (1960).

[2] Presented before the Division of Organic Chemistry at the Combined Southeastern-Southwestern Regional Meeting of the American Chemical Society, New Orleans, La., December, 1961.

[3] Chemistry Department, Villanova University, Villanova, Pa.

[4] This paper has been taken from the Doctorate thesis of Walter W. Zajac, Jr., and the Masters thesis of Louis G. Mahone presented to the Virginia Polytechnic Institute in 1959 and 1961, respectively.

[5] This investigation was supported by a research grant (AP-88) from the Division of Air Pollution, Bureau of State Services, Public Health Service.

[6] M. Katz, *Occupational Health Rev.*, **14**, 3 (1962); M. O. Amdur, *New Engl. J. Med.*, **266**, 555 (1962); W. McDermott, *Sci. Am.*, **205**, 49 (1961); M. R. Purvis, S. Miller, and R. Ehrlich, *J. Infect. Diseases*, **109**, 238 (1961); *Japan. Heart J.*, **2**, 180 (1961); J. Cuthbert, *Public Health* (London), **74**, 123 (1960); E. Gorham, *Med. Officer* (London), **101**, 178 (1959).

[7] E. L. Wynder, F. R. Lemon, and I. J. Bross, *Cancer*, **12**, 1016 (1959); P. Stocks, *Brit. J. Cancer*, **14**, 397 (1960); L. Kreyberg, *ibid.*, **13**, 618 (1959); H. L. Falk, P. Kotin, and A. Miller, *Intern. J. Air Pollution*, **2**, 201 (1960).

[8] F. A. Vingiello and W. W. Zajac, Jr., *J. Org. Chem.*, **26**, 2228 (1961).

[9] See, for example, M. Orchin and R. Friedel, *J. Am. Chem. Soc.*, **68**, 573 (1946); P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, 1689 (1960); E. Clar and M. Zander, *ibid.*, 1861 (1958).

[10] J. Cook, *ibid.*, 1592 (1933).

[11] A. Zincke and E. Ziegler, *Ber.*, **74**, 115 (1951).