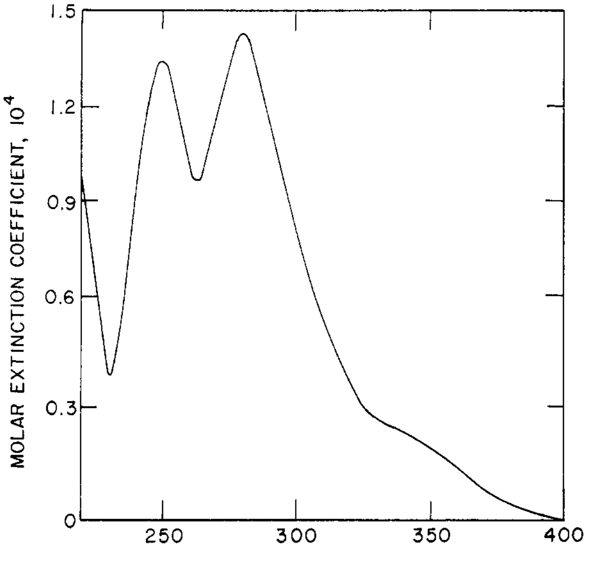

Fig. 2.—Ultraviolet absorption spectra of 3(2′-diisopropylvinylamino)indole in acetonitrile.

recrystallization from methanol–ether and dry acetone, analysis indicated contamination with trimethylammonium iodide and the compound was not investigated further. All other attempts to prepare stable salts from these enamines were unsuccessful.

Attempts to reduce 3-(2′-dimethylaminovinyl)-indole by catalytic hydrogenation to N,N-dimethyltryptamine were unsuccessful, but reduction with sodium borohydride in methanol or with lithium aluminum hydride in ether resulted in the formation of N,N-dimethyltryptamine which was identified by comparison of R_f values on thin layer chromatography (Silica Gel-G), color reaction (Ehrlich's) and infrared spectrum with those of authentic N,N-dimethyltryptamine.

Catalytic debenzylation of 5-benzyloxy-3-(2′-dimethylaminovinyl)indole in benzene with palladium on charcoal and hydrogen did not lead to the desired product (II).

Experimental[11]

5-Benzyloxy-3-indoleacetaldehyde was prepared by the method of Gray[7] from 5-benzyloxytryptophan.[12] A benzene solution of the aldehyde was mixed with a saturated sodium sulfite solution. The resulting bisulfite addition compound was recrystallized from water–ethanol. Liberation of the aldehyde with sodium carbonate solution gave a yellow oil (infrared absorption spectrum (neat): NH 2.85 μ, C=O 5.80 μ) which was characterized as the semicarbazone, m.p. 150–151°, recrystallized from methanol-water.

Anal. Calcd. for $C_{18}H_{18}N_4O_2$: C, 67.05; H, 5.61; N, 17.38. Found: C, 67.07; H, 5.78; N, 16.80.

Preparation of 3-(2-Disubstituted Aminovinyl)indoles.—The free aldehydes were prepared directly before use by liberation from the bisulfite addition compounds with sodium carbonate, and simultaneous extraction into ether. The ether was dried over sodium sulfate and then removed *in vacuo.* To 0.01 mole of aldehyde in 30–50 ml. of dry thiophene-free benzene in a reflux apparatus containing a Bidwell-Sterling moisture trap[7] and magnetic stirrer was added a solution of 0.012–0.02 mole of amine in 15 ml. of benzene. The reaction was warmed slowly and then refluxed for 2–3 hr. The benzene was evaporated and the residue purified as described under the individual amines. The amines were stored in a desiccator, preferably under nitrogen.

3-(2′-Dimethylaminovinyl)indole was obtained as an unstable oil after treatment of a benzene solution of the condensation product with Norit followed by evaporation of the benzene *in vacuo.*

Infrared absorption spectrum ($HCCl_3$): N—H 2.84 μ, C=C 6.07 μ vs. $\lambda_{max}^{acetonitrile}$ 245 mμ, 276 mμ, 325 mμ shoulder; ϵ_{max} 10,000; 9400; 3500.

5-Benzyloxy-3-(2′-dimethylaminovinyl)indole was obtained as an unstable brown oil. Infrared absorption spectrum (neat): N—H 2.78 μ, C=C 6.08 μ vs. $\lambda_{max}^{acetonitrile}$ 248 mμ shoulder, 278 mμ, 315 mμ shoulder; ϵ_{max} 7600; 8100; 3400.

3-(2′-Piperidinovinyl)indole was obtained as an unstable light brown oil. Infrared absorption spectrum (neat): N-H 2.79 μ, C=C 6.09 μ vs. $\lambda_{max}^{acetonitrile}$ 245 mμ shoulder; 278 mμ, 325 mμ shoulder; ϵ_{max} 10,100; 10,800; 3400.

3-(2′Dibenzylaminovinyl)indole was recrystallized from dry ether containing a trace of triethylamine yielding white crystals, m.p. 128.5–130°; yield 12%. The crystals turned tan within a week. Infrared absorption spectrum (KBr): N-H 2.80 μ C=C 6.10 μ vs. $\lambda_{max}^{acetonitrile}$ 246 mμ, 272 μ, 310 mμ shoulder; ϵ_{max} 12,00; 9600; 5030.

Anal. Calcd. for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.06; H, 6.76; N, 7.91.

5-Benzyloxy-3-(2′-dibenzylaminovinyl)indole was recrystallized from ether containing a trace of trimethylamine as white crystals, yield 15%, m.p. 139–141°, which became tan on standing. Infrared absorption spectrum ($CHCl_3$): N-H 2.70 μ C=C 6.10 μ vs. $\lambda_{max}^{acetonitrile}$ 245 mμ, 258 mμ, 279 mμ, 330 mμ shoulder; ϵ_{max} 15,400; 95,400; 16,100; 5100.

Anal. Calcd. for $C_{31}H_{28}N_2O$: C, 83.75; H, 6.36; N, 6.30. Found: C, 83.24; H, 6.53; N, 5.98.

3-(2′-Diisopropylaminovinyl)indole was recrystallized from dry ether containing a trace of triethylamine as light tan crystals, m.p. 129–132°, yield 25%. Infrared absorption spectrum ($HCCl_3$): N-H 2.82 μ. C=C 6.09 μ vs. $\lambda_{max}^{acetonitrile}$ 250 mμ, 280 mμ, 338 shoulder; ϵ_{max} 11,600; 13,200; 2800.

Anal. Calcd. for $C_{16}H_{22}N_2$: C, 79.34; H, 9.09; N, 11.57. Found: C, 78.93; H, 8.45; N, 11.37.

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[11] The skillful cooperation of the Regis Chemical Co. under a Psychopharmacology Service Center Contract is gratefully acknowledged.

[12] A. Ek and B. Witkop, *J. Am. Chem. Soc.*, **75**, 500 (1953).

Photochemical Reactions. XI. Diphenylacetylene[1-3]

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Photochemical dimerization of substituted olefins represents a convenient method for the preparation of certain cyclobutanes. In analogy, sub-

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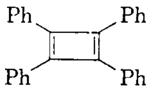
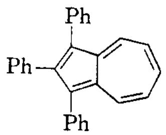
stituted acetylenes should be susceptible to dimerization and give cyclobutadienes or their transformation products. Irradiation of diphenylacetylene (I) in hexane solution with a Hanau "Labortauchlampe S81" gave 1,2,3-triphenylazulene[4] (III), 1,2,3-triphenylnaphthalene[5] (IV), hexaphenylbenzene[6] (V), and a colorless, extremely insoluble compound, m.p. 427–429°. The infrared spectrum of this substance was identical to that of a hydrocarbon, m.p. 425–427°, prepared later in far superior yield by thermal decomposition of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide[7] and by reaction of I with phenylmagnesium bromide.[8] It seems to be a tetramer of diphenylacetylene and expression VI has been proposed.[9] The following, *purely speculative* scheme accounts for the formation of the various photoproducts. Photodimerization of I may produce tetraphenylcyclobutadiene[10] (II) which according to theoretical considerations is a triplet in the ground state.[11]

Ph—C≡C—Ph

I



II



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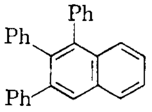

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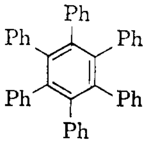

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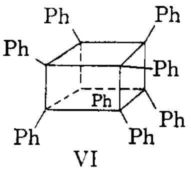
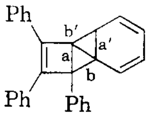
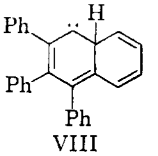


VI



VII



VIII

This intermediate may subsequently dimerize to yield VI, combine with starting material to give hexaphenylbenzene (V), and finally undergo bond redistribution. The resulting substituted bicyclobutane[12] (VII) is not expected to be stable at room temperature and of the various bond breaking processes those producing strain free rings should be favored. Homolysis at a and a′ gives the azulene (III) while an alternate process at b and b′ regenerates tetraphenylcyclobutadiene (II). Cleavage of geminal bonds in the bicyclobutane (VII) results in the generation of carbenes and of the four isomers formally possible only one, VIII, contains no small ring. Conversion to the naphthalene (IV) is terminated by hydride shift. The feasibility of the bond redistribution reaction leading to VII is being investigated experimentally.

Experimental[13]

Diphenylacetylene, m.p. 60–61° (17 g.) dissolved in pure hexane (50 ml.) was irradiated for 1 week. "Prepurified" nitrogen was bubbled through the solution and the apparatus was cooled to 15–30° using a water bath. The reaction mixture was filtered to remove insoluble material (A, 92 mg.) and the filtrate was concentrated to a green solid. Recrystallization from ethanol (50 ml.) removed the bulk of unchanged starting material and the mother liquor was chromatographed in hexane solution over a column of "Davison 923" silica gel. Elution with the same solvent gave I (total recovery 16.0 g.). Further elution with hexane containing 5% benzene yielded 1,2,3-triphenylnaphthalene (IV) (172 mg.), m.p. 151–153° pure and mixed with an authentic sample (superimposable infrared spectra in potassium bromide pellets). Later fractions contained a blue substance (151 mg.) which after recrystallization from ether–pentane had m.p. 214–216°. A mixture of it and an authentic sample of 1,2,3-triphenylazulene (III) m.p. 216–217° melted at 214–217° and the infrared spectra (in potassium bromide) of the two samples were superimposable. The insoluble material (A) mentioned above was washed on a filter with chloroform and then with hot nitrobenzene. A colorless, crystalline compound (6 mg.), m.p. 437–439°, remained on the filter whose infrared spectrum (in potassium bromide) was identical with that of authentic hexaphenylbenzene (V), m.p. 439–441°, and a mixture of the two had m.p. 439–440°. When the nitrobenzene filtrate was poured into benzene (30 ml.), a colorless substance (11 mg.) precipitated which had m.p. 427–429°. Its infrared spectrum was different from that of hexaphenylbenzene (V) and a mixture of the two had m.p. 400–430°. As mentioned in the discussion section, this new hydrocarbon is identical with a substance prepared by a different route and believed to be octaphenylcubane (VI).

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(3) First presented in a lecture to the Swiss Chemical Society in Basel [*Chimia* (Aarau), **12**, 282 (1958)].

(4) S. J. Assony and N. Kharasch, *J. Am. Chem. Soc.*, **80**, 5978 (1958); R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); N. R. Slobotkin, *J. Org. Chem.*, **25**, 273 (1960). We wish to thank Professor N. Kharasch for an authentic sample of this substance.

(5) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

(6) W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

(7) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961). We are indebted to Dr. H. H. Freedman for this information.

(8) M. Tsutsui, *Chem. Ind.* (London), 780 (1962).

(9) H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962).

(10) Tetraphenylcyclobutadiene iron tricarbonyl [W. Hubel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960)] and nickel bromide complexes[7] are known but there is no published evidence to support the suggestion [A. T. Balaban, *Tetrahedron Letters*, **5**, 14 (1959)] that a hydrocarbon m.p. 154–155° prepared by Kharasch (ref. 4) is tetraphenylcyclobutadiene.

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(12) A few bicyclobutanes are known: K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5262 (1959); W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

(13) Melting points are uncorrected.