during one hour from +2.40° to +0.06° and remained unchanged upon further boiling. This corresponds to a specific rotation of +3° for the dimethylglucose in water (c 2). The resin was removed by filtration and the water evaporated in vacuum. It was dried over P_2O_5, leaving 490 mg. of colorless sirup which failed to crystallize.

The freshly hydrolyzed solutions were strongly reducing toward alkaline hypoiodite, Hagedorn–Jensen[5] solution and hot Fehling solution. They would not, however, reduce Fehling solution in the cold, nor restore color to a decolorized fuchsin–sulfurous acid solution. The sirups obtained after evaporation of the water showed greatly decreased reducing activity, but the reduction was restored upon boiling the sirups in dilute acid solution.

A drop of the freshly hydrolyzed 2,5-dimethylglucofuranose solution was placed on a strip of filter paper which was then developed as a descending chromatogram with the butanol–formic acid and water reagent of Wiggins and Williams.[6] The substance, moving as a single spot, travelled 5 or 6 times as far as glucose under comparable conditions. The color of the spot was developed with aniline hydrogen phthalate. Both the unhydrolyzed glucoside and the sirup obtained after hydrolyzing and drying failed to give a color with the aniline hydrogen phthalate reagent, but after hydrolysis with dilute acid both gave the same fast-moving dimethylglucose.

Acknowledgment.—The micro carbon and hydrogen analyses were performed by Lawrence E. Brown, and the methoxyl analyses by J. W. Weaver. Laurence W. Mazzeno, Jr., assisted with the reducing sugar determinations and E. A. Schoenhardt, Jr., with the paper chromatography.

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[5] C. S. Hanes, *Biochem. J.*, **23**, 99 (1929).

[6] L. F. Wiggins and J. H. Williams, *Nature*, **170**, 279 (1952).

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Reactions of Diazo Compounds with Nitroölefins. IV. The Decomposition of Diphenyldiazomethane

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The reaction of diphenyldiazomethane with nitroölefins to give nitropyrazolines[2] is complicated, in certain cases, by decomposition of the diazocompound. For example, it was found that diphenyldiazomethane does not react with 1-phenyl-2-nitropropene-1 to give the expected pyrazoline. When the reaction was carried out in benzene, only benzophenone azine, a known decomposition product of diphenyldiazomethane,[3] and unreacted nitroölefin were obtained. When hot petroleum ether was employed as solvent, *sym*-tetraphenylethane and a molecular complex of this substance and benzophenone azine were obtained in addition to benzophenone azine and starting material. Neither *sym*-tetraphenylethane nor the molecular complex described had previously been reported as decomposition products of diphenyldiazomethane. That they were not derived from the nitroölefin was shown by the isolation of the same products from similar reactions conducted in the absence of the olefin.

Isolation of *sym*-tetraphenylethane from reactions employing hot petroleum ether as solvent, and failure to obtain this product from reactions employing benzene as solvent or reactions effected without solvent, suggested the following course for the decomposition of the diazo compound.

$$(C_6H_5)_2CH_2N_2 + \underset{\text{I}}{(C_6H_5)_2C:}$$

$$\text{I} \xrightarrow{\text{solvent}} (C_6H_5)_2CH\cdot \longrightarrow \underset{\text{II}}{(C_6H_5)_2CHCH(C_6H_5)_2}$$

There was no evidence for the formation of tetraphenylethylene[4] which might be expected to result directly from I.

Evidence which constitutes proof of structure of the molecular complex of *sym*-tetraphenylethane and benzophenone azine is described in the Experimental section. Examination of the ultraviolet spectra of the molecular complex indicated that there was no interaction between the two components in dilute solution in ethanol. At each wave length the extinction coefficient was the sum of those of its components. Jones and Neuworth[5] reported a similar behavior for the 1,3,5-trinitrobenzene derivatives of naphthalene, anthracene, etc.

Experimental

Attempts to Add Diphenyldiazomethane to 1-Phenyl-2-nitropropene-1.—The results are summarized in Table I. In each case 1.60 g. (0.0098 mole) of olefin was treated with 2.20 g. (0.0113 mole) of diphenyldiazomethane. The reactions were allowed to proceed until the red color of the diazo compound disappeared. The products were separated by crystallization from petroleum ether, and further purified by recrystallization from petroleum ether, benzene or ethanol.

TABLE I

Run	Solvent	Temp., °C.	Time of reacn.	Benzophenone azine, m.p. 162–164°, g.	*sym*-Tetraphenylethane, m.p. 211–212°, g.	Molecular complex, m.p. 177–177.5°, g.	Unchanged olefin, g.
1	Pet. ether	120	30 min.	0.50	0.15	0.05	. .
2	Pet. ether	55	9.5 days	.38	.05	.32	. .
3	Pet. ether	22	6 mo.	.90	. .	. .	0.10
4	None	22	1 mo.	.95	. .	. .	1.33

Decomposition of Diphenyldiazomethane in Benzene.—A solution of diphenyldiazomethane (2.7 g., 0.014 mole) in benzene (50 ml.) was heated at the reflux temperature until the red color of the diazo compound had disappeared (five days). The benzene was removed by distillation and the residual solid was recrystallized from ethanol. There was obtained 2.0 g. (74% yield) of benzophenone azine, m.p. 163–163.5°. Neither *sym*-tetraphenylethane or the complex of azine and hydrocarbon could be detected in the reaction product.

Decomposition of Diphenyldiazomethane in Petroleum Ether.—A solution of diphenyldiazomethane (4.7 g., 0.024 mole) in petroleum ether was heated at 120° (reflux) for 2.5 hours (the red color disappeared after 90 minutes). The mixture was cooled and 1.9 g. (45% yield) of yellow crystals, m.p. 157–173°, was removed by filtration. The solid melted at 177–177.5° after recrystallization from ethanol and did not depress the melting point when admixed with the 1:1 molar complex of benzophenone azine and *sym*-tetraphenylethane.

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[1] From the Ph.D. Thesis of William R. Hasek, University of Minnesota, 1953.

[2] W. E. Parham and W. R. Hasek, THIS JOURNAL, **76**, 799 (1954).

[3] T. Curtius and F. Rauterberg, *J. prakt. Chem.*, [2] **44**, 192 (1891).

[4] Benzophenone azine has been previously reported as the only product resulting from the decomposition of diphenyldiazomethane. However, di-(p-methoxyphenyl)-diazomethane and 9-diazofluorene give tetra-(p-methoxyphenyl)-ethylene and difluorenylidene, respectively. *Cf.* H. Staudinger and O. Kupfer, *Ber.*, **44**, 2197 (1911).

[5] R. C. Jones and M. B. Neuworth, THIS JOURNAL, **66**, 1497 (1944).

Degradation and Synthesis of the Molecular Complex.—When a sample of the molecular complex (m.p. 177–177.5°) was dissolved in warm benzene and the solution was cooled, white crystals melting at 211–212° were obtained. This product did not depress the melting point when admixed with samples of *sym*-tetraphenylethane (m.p. 211–212°). The benzene filtrate, from which *sym*-tetraphenylethane had been removed, was evaporated to dryness and the residue was recrystallized from ethanol. Benzophenone azine, m.p. 162–164°, was obtained.

Separate solutions containing equimolar amounts of benzophenone azine and *sym*-tetraphenylethane in ethanol were mixed and the resulting solution was cooled. Yellow crystals, m.p. 177–177.5°, were obtained. A mixed melting point of this product and the molecular complex described above was 177–177.5°.

Anal. Calcd. for $C_{52}H_{42}N_2$: C, 89.9; H, 6.09. Found: C, 89.9; H, 5.85.

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2-Bromophenanthridone

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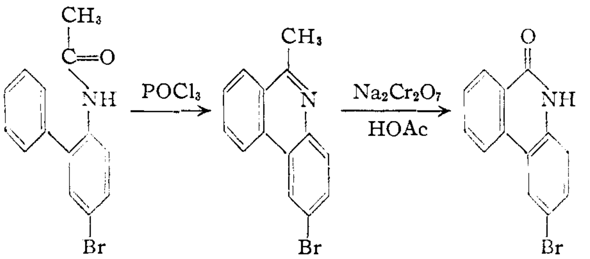
In 1935, Walls[1] recorded the preparation of 2-bromophenanthridone (III) by the cyclization of 2-acetamido-5-bromobiphenyl (I) and oxidation of the resulting 2-bromo-6-methylphenanthridine (II).

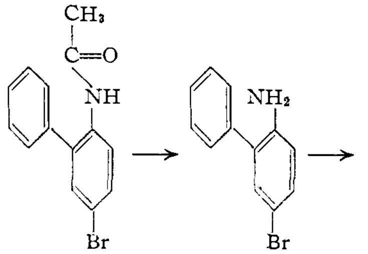


I II III

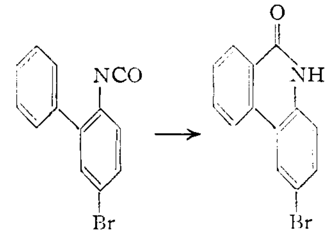
Walls described III (after recrystallization from nitrobenzene) as yellow needles which decomposed at 302° after previous sintering.

In the course of preparing some phenanthridone derivatives we found that treatment of phenanthridone in acetic acid with bromine resulted in a nearly quantitative yield of a monobromo derivative. The product recrystallized from nitrobenzene in white fluffy needles, m.p. 323.5–324.5°. This product was thought to be the 4- or, more likely, the 2-bromo derivative (III).

In view of the discrepancy in melting points, and as there appeared to be no reason to expect III to have the yellow color ascribed to it by Walls, an unambiguous synthesis of III was effected.



I IV



V III

The melting point of this product agrees with that of the product obtained by the bromination of phenanthridone, and a mixed melting point shows no depression. It would thus seem quite well established that the two are identical, and that the product described by Walls was impure.

Since slight modifications in the preparation of 2-biphenylyl isocyanate described by Fraenkel-Conrat and Olcott,[2] and in the cyclization of this to phenanthridone described by Butler,[3] have resulted in nearly quantitative yields, an over-all yield of 92–93% of III from 2-aminobiphenyl may be attained. It is of interest that, contrasted with the nitration of phenanthridone,[4] bromination shows no evidence of the formation of the 4-substituted isomer.

Experimental[5]

2-Biphenylyl Isocyanate.—A solution of 300 g. of 2-aminobiphenyl in 500 ml. of toluene was added slowly with stirring under reflux to a solution of 700 g. of phosgene in 2000 ml. of toluene. A crystalline precipitate formed. The mixture was stirred and refluxed for five hours, then allowed to stand overnight. The resulting clear brown solution was stripped of solvent and distilled *in vacuo* to give 345 g. of product (99.7% yield), b.p. 92–94° (1 mm.) (lit.[2] b.p. 100° (0.5–1.0 mm.)).

Phenanthridone.—In a 2-liter, 3-necked flask equipped with addition funnel, solid addition tube, reflux condenser and stirrer, was placed 1000 ml. of chlorobenzene. While the flask was cooled in ice to keep the temperature of the reaction mixture at about 30°, 244 g. (1.25 moles) of 2-biphenylyl isocyanate and 175 g. (1.30 moles) of powdered anhydrous aluminum chloride were added at approximately equivalent rates. When the reactants had been added the mixture was stirred with continued cooling for a half hour, then for a few minutes at room temperature. The mixture was filtered; the solid was washed with a little chlorobenzene and dried overnight at room temperature. The dry product was hydrolyzed by beating in a Waring Blendor with warm very dilute hydrochloric acid. The slurry was filtered; the solid was rebeaten with methanol and refiltered, washed with methanol and dried. The yield of pure white phenanthridone, m.p. 291.5–293° (lit.[3] 292.5–293.5°), was 233 g. (95.5%).

A. **2-Bromophenanthridone by Bromination. 2-Bromophenanthridone (III).**—To a stirred, refluxing solution of 19.5 g. (0.10 mole) of phenanthridone in 200 ml. of glacial acetic acid was added dropwise a solution of 17.6 g. (0.11 mole) of bromine in 50 ml. of glacial acetic acid over a period of about 1.5 hours. After a short induction period, a copious evolution of hydrogen bromide (trap!) was evident, and a white precipitate began to form. When all of the bromine had been added, the mixture was stirred and refluxed until the orange bromine color was no longer noticeable (about 20 minutes), then poured into water and filtered. The white filter cake was washed well with water

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[1] L. P. Walls, *J. Chem. Soc.*, 1405 (1935).

[2] H. Fraenkel-Conrat and H. S. Olcott, THIS JOURNAL, **66**, 845 (1944).

[3] J. M. Butler, *ibid.*, **71**, 2578 (1949).

[4] A. J. Nunn, K. Schofield and R. S. Theobald, *J. Chem. Soc.*, 2797 (1952).

[5] The author wishes to thank Mr. O. E. Sundberg, Miss I. H. Prokul and Mrs. R. Cran for the microanalyses. All melting points were taken in commercially available soft glass capillaries, using Anschütz thermometers and a Hershberg apparatus.