TABLE III

β-KETOESTERS (II) $RCH_2COCH_2COOC_2H_5$

R	B.p., °C.	Mm.	$n^{25}D$	Yield, %	Analyses, % Calcd. C	Calcd. H	Found C	Found H
a	117–120	2	1.5172	28	[a] B.p. 126–128 (4 mm.), $n^{22}D$ 1.5130			
b	152–163	4	1.5011	60	70.89	7.32	70.82	7.50
c	140–170[b]	0.3	1.5086	51	67.18	7.25	67.00	7.49
d	120–170[b]	.025	1.5083	58	67.18	7.25	66.98	7.13
e	160–191[b]	.02	1.5151	55	63.63	6.10	63.70	6.31

[a] D. Libermann, I. Himbert, L. Hengl and G. Kirchoffer, *Compt. rend.*, **229**, 765 (1949). [b] Bath temperature.

TABLE IV

SUBSTITUTED CYCLOPENTENOLONES

Derivative	R	Formula	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
3,5-Dinitrobenzoate	a	$C_{19}H_{14}N_2O_7$	166–167	59.69	3.69	7.33	59.75	3.58	7.22
	b	$C_{20}H_{16}N_2O_7$	196–197	60.60	4.07	7.07	61.00	3.82	6.97
p-Nitrobenzoate	c	$C_{21}H_{19}NO_6$	115–116	66.13	5.02	3.68	66.18	5.24	3.96
	d	$C_{21}H_{19}NO_6$	157.5–158.5	66.13	5.02	3.68	66.13	5.08	3.99
	e	$C_{21}H_{17}NO_7$	139.5–140.5	63.79	4.34	3.54	63.28	4.75	3.79

ether and extracted consecutively with five 50-ml. portions of nitromethane (redistilled at 30 mm. pressure). The nitromethane solutions were passed through a column 12 mm. in diameter and 30 mm. long of charcoal (Norite A) that had been wetted with nitromethane, and the initial heat was permitted to dissipate (charcoal heats up when wetted with nitromethane). Care was taken not to let the charcoal get dry between successive aliquots. An 80 mm. vacuum was applied to facilitate the flow through the column.

The first 25 ml. of solution to pass through the column was set aside. The next 100 ml., which contained most of the ester, was placed in a modified Claisen distilling flask[16] and the nitromethane removed under 20 mm. vacuum with a water-bath at 40–50°. When most of the nitromethane was gone, the water-bath was removed and the vacuum maintained for four hours. Dry nitrogen was passed through the ebullition tube at all times to avoid oxidation of the ester. A vacuum of 0.5 mm. drawn through a Dry Ice trap was applied to the residual ester for eight hours at 30° while spread out in a thin layer at the bottom of flask; yield 3.8 g.

Results of analysis, yields and refractive indices of the respective esters (VII) of chrysanthemic acid are given in Table I.

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[16] W. F. Barthel, *Ind. Eng. Chem., Anal. Ed.*, **16**, 374 (1944).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH SECTION, PICATINNY ARSENAL]

Identification of Isomers Formed in the Nitration of Carbazole[1]

BY D. B. MURPHY, F. R. SCHWARTZ, J. P. PICARD AND J. V. R. KAUFMAN

RECEIVED APRIL 13, 1953

Direct nitration of carbazole results in the formation of two isomeric compounds. One of these is 1,3,6,8-tetranitrocarbazole. The other, present to the extent of about 10% in the crude product, is believed to be the 1,2,6,8-isomer and evidence is presented in support of this belief.

Several investigators,[2,3,4] in describing the preparation of tetranitrocarbazole, report the separation, by fractional crystallization from acetic acid, of a number of isomers from the products of nitration. The isomer formed in largest amount was later shown to be 1,3,6,8-tetranitrocarbazole.[5] No attempt to determine the structures of the other isomers is recorded, and, considering the techniques used, it is possible that no really effective separation of the products of this reaction has ever been accomplished. The work described here was undertaken with the intention of determining whether a mixture of isomers is formed in the nitration of carbazole, and, if so, of establishing the structures of these isomers.

From a sample of crude tetranitrocarbazole prepared by sulfonation and subsequent nitration of carbazole[6] three fractions, varying in their solubilities, could be separated by repeated fractional crystallization from acetone. The most soluble of these fractions, obtained in small amount, contained about 13% nitrogen, compared with the calculated value of 20.17% for tetranitrocarbazole. Based upon this analysis and the poor resolution obtained in the infrared spectrum of this substance, we believe this to be a mixture of decomposition and condensation products formed in the reaction, together with partially nitrated material. Both the middle fraction and the least soluble fraction, melting at 253–254° and 295–296.0°, respectively, after recrystallization, had nitrogen contents close to the calculated value for tetranitrocarbazole, indicating that they were isomers.

The least soluble fraction was considered most likely to be the 1,3,6,8-isomer, and we accordingly

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[1] Presented at the Meeting-in-miniature of the North Jersey Section, A.C.S., January 26, 1953.

[2] G. L. Ciamician and P. P. Silber, *Gazz. chim. ital.*, **12**, 272 (1882).

[3] R. Escales, *Ber.*, **37**, 3596 (1904).

[4] H. Raudnitz, *ibid.*, **60**, 743 (1927).

[5] W. Borsche and B. G. B. Scholten, *ibid.*, **50**, 596 (1917).

[6] Casella and Co., German Patent 268,173; French Patent 464,-538.

set out to prepare an authentic sample for comparison. Borsche and Scholten[5] had prepared 3,3′,5,5′-tetranitro-2,2′-dimethoxybiphenyl. Heating this in a sealed tube with alcoholic ammonia formed the corresponding tetranitrocarbazole. Since their initial nitration step could have led to a mixture of isomers, and since a compound was desired whose structure was known without question, a method was followed which could lead only to the 1,3,6,8-isomer.

2,4-Dinitrophenol was iodinated and then treated with diazomethane to give 6-iodo-2,4-dinitroanisole. 3,3′,5,5′-Tetranitro-2,2′-dimethoxybiphenyl was prepared from this compound by the Ullmann reaction, and this, in turn, was converted to 1,3,6,8-tetranitrocarbazole by heating it in a sealed tube with alcoholic ammonia.

The product, after recrystallization from acetic acid, melted at 295.6–296.0°. A mixed melting point with the least soluble fraction of crude tetranitrocarbazole showed no depression, and the infrared absorption spectra of these two substances were identical.

It has been claimed[7] that the product formed by sulfonating carbazole with oleum is carbazole-2,3,6,8-tetrasulfonic acid. It seemed reasonable that in the ordinary nitration of carbazole a certain amount of this substance might be formed. Upon nitration, this would be expected to give the corresponding 2,3,6,8-tetranitrocarbazole. Accordingly, carbazole was sulfonated with 30% fuming sulfuric acid and then nitrated in the usual manner. In this way, a product was obtained whose melting point and infrared absorption spectra were identical with those of the middle fraction from extraction of crude tetranitrocarbazole. At first this was assumed to be 2,3,6,8-tetranitrocarbazole.

The structure of the 1,3,6,8-tetranitrocarbazole is evident from its synthesis; that of the second isomer, however, is not established by its method of preparation, although it has been observed to dissolve in hot, dilute sodium sulfite solution, indicating the presence of adjacent nitro groups.[8]

It is well established that infrared absorption bands arising from the out-of-plane hydrogen bending modes are located between 10 and 14 μ.[9,10] Their positions are determined largely by the relationship of the hydrogen atoms to one another and, in general, is independent of the nature of other substituents.

Examination of the structures of the 1,3,6,8- and 2,3,6,8-isomers shows that in both cases, all of the hydrogens are isolated from one another. For this reason, one would expect the spectra of the 1,3,6,8- and the so-called 2,3,6,8-isomers to be essentially the same in the region from 11 to 14 μ. This is not found to be the case; a pronounced new band is found at 12.15 μ in the spectrum of the "2,3,6,8-" isomer. This band may well be attributed to the bending modes of two adjacent hydrogen atoms.

The presence of a sulfonic acid group in the 2-position of the carbazoletetrasulfonic acid from which the "2,3,6,8-" tetranitrocarbazole was prepared seems fairly certain.[11] It seems reasonable to believe then that upon nitration of this material, one of the nitro groups will enter the 2-position. The second nitro group must then be in either the 1- or 3-position in order for the tetranitrocarbazole to dissolve in aqueous sodium sulfite. If two hydrogen atoms are to be adjacent to one another, as required by the interpretation of the infrared spectrum, the second nitro group must be located in position one.

In view of these facts, the 1,3,6,8- and 1,2,6,8-structures are suggested for the above isomers of tetranitrocarbazole.

Experimental[12]

Nitration of Carbazole.—Three hundred thirty-four grams of carbazole was added in small portions and with vigorous stirring to 1050 ml. of sulfuric acid, keeping the temperature between 30 and 50°. The temperature was then raised to 70–80° and held there until a drop of the solution did not form a precipitate when added to a few drops of water. The solution was then cooled and added dropwise with stirring to 1003 g. of 94% nitric acid kept at 30–40°. The temperature was then raised to 78° and kept there for two hours to complete nitration. On cooling, the solution was added to several volumes of ice and water; the solid was then filtered, boiled several times with water until the water was neutral to litmus and finally dried at 100°.

6-Iodo-2,4-dinitrophenol.—Fourteen grams of 2,4-dinitrophenol was dissolved in about 300 ml. of glacial acetic acid in each of four flasks set in a shaking machine. The flasks were shaken vigorously, and to each was added, alternately and in small portions, 15 g. of fresh yellow mercuric oxide and 21 g. of finely powdered iodine. The flasks were shaken after each addition until all of the iodine was consumed before more was added, and finally for about one hour after addition was complete. The solutions were then filtered, combined, and added to several volumes of water. The product which precipitated was freed from mercuric iodide by being thoroughly triturated with 50% potassium iodide solution, after which it was filtered and washed with water. Recrystallization was unnecessary; yield 79.2 g. (84.5%), m.p. 106–107°.

Anal. Calcd. for $C_6H_3C_4N_2I$: N (nitro), 9.04. Found: N (nitro), 9.01.

3,3′,5,5′-Tetranitro-2,2′-dimethoxybiphenyl.—This was prepared by a modification of the method of Case and Schock.[13] Seven grams of 6-iodo-2,4-dinitroanisole, prepared in quantitative yield from the corresponding phenol by treatment with diazomethane in benzene, was added to 15 ml. of gently boiling nitrobenzene. Six grams of copper powder (Fisher Scientific Company, electrolytic dust, C.p.) was then added in small portions over a 15-minute period. Reflux was continued for 45 minutes and the mixture was then cooled and filtered. The flask and copper powder were thoroughly washed with acetone, and the washes added to the original solution. The whole solution was then boiled 10 or 12 times with fresh portions of Norit until light brown. The acetone was removed on a steam-bath, 50 ml. of benzene and 400 ml. of petroleum ether were then added and the mixture was cooled on ice. After standing several hours, 0.53 g. (12.5% yield) of bright yellow needles was obtained, melting at 169–171°. The product was recrystallized by dissolving it in acetone, boiling with Norit,

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[7] A. Bergdolt and A. Schmelzer, U. S. Patent 1,981,301.

[8] Advantage is taken of this characteristic of compounds possessing labile nitro groups in the removal of unsymmetrical isomers from crude TNT (see T. L. Davis, "The Chemistry of Powder and Explosives," John Wiley and Sons, New York, N. Y., 1943, p. 146). 1,3,6,8-Tetranitrocarbazole was unaffected by sodium sulfite solution. Ordinary crude tetranitrocarbazole (m.p. 278°) lost about 10% of its weight when similarly treated, and the melting point of the residue was found to have been raised to that of the pure 1,3,6,8-isomer.

[9] H. W. Thompson, *J. Chem. Soc.*, 328 (1948).

[10] N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

[11] Although Bergdolt and Schmelzer claimed to have prepared carbazole-2,3,6,8-tetrasulfonic acid, a reasonably adequate proof is offered only for the presence of a sulfonic acid group in the 2-position (see ref. 7).

[12] All melting points are corrected.

[13] F. H. Case and R. V. Schock, THIS JOURNAL, **65**, 2086 (1943).

filtering and adding petroleum ether. The recrystallized material exhibited dimorphism, melting at 178.3°, resolidifying and melting again at 191°.[14]

Anal. Calcd. for $C_{14}H_{10}O_{10}N_4$: C, 42.64; H, 2.54. Found: C, 42.59; H, 2.49.

1,3,6,8-Tetranitrocarbazole.—9.57 g. of 3,3′,5,5′-tetranitro-2,2′-dimethoxybiphenyl was heated four hours at 135° in a sealed tube with 35 ml. of absolute alcohol saturated with ammonia. 0.22 g. of red-brown needles (44% yield) were filtered from the solution left in the tube and washed with acetone. After recrystallization from glacial acetic acid, the product was obtained as pale yellow, transparent needles melting at 295.6–296.0°.

Anal. Calcd. for $C_{12}H_5O_8N_5$: C, 41.50; H, 1.44. Found: C, 41.69; H, 1.24.

1,2,6,8-Tetranitrocarbazole.—Fifty grams of carbazole wera dissolved in 300 g. of fuming (30% SO_3) sulfuric acid, keeping the temperature at 40–50°. The mixture was then heated about two hours at 90–100°. After this heating period, there was still a large amount of solid present, but the mixture was completely water soluble. One hundred sixty grams of 93% nitric acid was then added slowly, keeping the temperature between 40–60°. The mixture was then filtered through a fritted glass funnel, and the solid was washed with water and dried. One gram of the crude product, melting at 230–234°, was dissolved in 25 ml. of boiling nitrobenzene. The solution was cooled, filtered, and 50 ml. of benzene was added. After a time, the pure 1,2,6,8-tetranitrocarbazole separated in small, glistening yellow plates, m.p. 153–154°.

Anal. Calcd. for $C_{12}H_5O_8N$: C, 41.50; H, 1.44; N, 20.17. Found: C, 41.58; H, 1.39; N, 20.06.

Infrared Absorption Spectra.—Infrared spectra were obtained using a Perkin–Elmer double-beam infrared spectrophotometer. A mineral oil mull was used between 6.0–6.6 and 7.7 and 15.0 μ. Hexachlorobutadiene was used as the mulling agent between 2.0–6.0 and 6.6–7.7 μ.

DOVER, NEW JERSEY

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[14] J. Van Alphen, *Ber.*, **64**, 1819 (1931), reports 179 and 191°.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NOTRE DAME, AND THE RESEARCH DEPARTMENT OF THE LABORATORIES VIETA-PLASENCIA, HAVANA, CUBA]

Abnormal Chichibabin Reactions. The Condensation of Phenylacetaldehyde and Homoveratric Aldehyde with Ammonia[1]

BY ERNEST L. ELIEL,[2] RICHARD T. MCBRIDE[3] AND ST. KAUFMANN

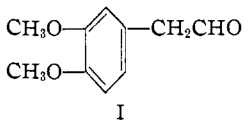
RECEIVED MARCH 14, 1953

The condensation of homoveratric aldehyde (I) with ammonia in boiling ethanol solution gives rise to a base whose structure has been proved to be 3,5-diveratrylpyridine (II). When the condensation is carried out in an autoclave under pressure, the product is sometimes 3,5-diveratrylpyridine (II) and sometimes a base which appears to be 3,5-diveratryl-2-homoveratrylpyridine (III). Phenylacetaldehyde and ammonia react only in an autoclave at elevated temperatures to give 3,5-diphenylpyridine and toluene.

Several years ago,[4] in attempts to synthesize the alkaloid papaverine by novel methods, we had occasion to condense homoveratric aldehyde (3,4-dimethoxyphenylacetaldehyde, I) with ammonia. Reaction took place with surprising ease in boiling ethanol solution giving rise to a crystalline base, isolated after treatment of the reaction mixture with acid, which accounted for *ca.* 10% of the weight of the starting materials.

The base was different in properties from papaverine, and its analysis and molecular weight pointed to the formula $C_{21}H_{21}NO_4$ which contains one carbon atom more than can be accounted for by the condensation of two molecules of the aldehyde I with one molecule of ammonia. The infrared spectrum of the base indicated the absence of functional groups other than the expected methoxyl groups and suggested that the base was tertiary. These findings were corroborated by classification tests.

The new base was resistant toward hot permanganate in either acidic or basic solution. Boiling with nitric acid did not lead to oxidation, but yielded a crystalline dinitro derivative of the original compound. Treatment of the base with methyl iodide yielded a crystalline methiodide which by reaction with silver chloride slurry could be converted to a water-soluble methochloride. The same methochloride was produced when homoveratric aldehyde (I) was condensed with methylamine in boiling ethanol, and the reaction mixture treated with hydrochloric acid; it was converted to the less soluble methiodide by treatment with potassium iodide in aqueous solution.



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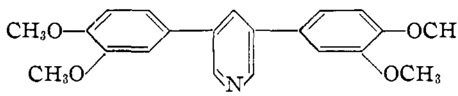

II

Oxidation of the methiodide with alkaline potassium permanganate (after conversion to the methonitrate by means of silver nitrate) gave veratric acid (3,4-dimethoxybenzoic acid) in such a yield as to suggest the presence of *two* methoxyl-substituted phenyl rings in the original base. This finding, coupled with the fact that pyrolysis of the quaternary hydroxide obtained from the methiodide regenerated the original base, suggested that the base was a diveratrylpyridine, and, in view of its method of formation, probably 3,5-diveratrylpyridine (3,5-bis-(3,4-dimethoxyphenyl)-pyridine, II). Formula II was corroborated by

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[1] This paper is taken in part from the Ph.D. dissertation of Richard T. McBride.

[2] To whom inquiries regarding this paper should be directed: University of Notre Dame, Notre Dame, Ind.

[3] Socony–Vacuum Fellow, 1951–1952; Reilly Fellow, 1952.

[4] This work was initiated in the Laboratories Vieta–Plasencia in 1945–1946. A few experiments were carried out at the University of Illinois in 1947 and the work was concluded at the University of Notre Dame, 1950–1952.