this was added a solution of 0.003 mole of chlorine in 10 ml. *o*-dichlorobenzene. A third solution of 0.1 to 0.3 g. of catalyst (aluminum bromide or gallium chloride) in 5 ml. of cold *o*-dichlorobenzene was added rapidly with stirring. A 5-ml. aliquot was then removed, washed with water, dried over magnesium sulfate, filtered, and used directly for gas chromatographic analysis.

Chlorination method D. Chlorine was bubbled through a solution of 0.01 mole of biphenyl or monochlorobiphenyl and 0.1 g. of catalyst ($SnCl_4$, antimony pentachloride, ferric chloride, or aluminum chloride) in 12 ml. of benzene at a rate which maintained the temperature at 40 ± 1°. Two-milliliter aliquots were taken at 5, 10 and 15 min. The aliquots were washed with water, dried over magnesium sulfate, filtered[2] and most of the solvent removed. The concentrate was used directly for gas chromatographic analysis.

Analytical procedure.[25] The analyses were performed on a Barber-Colman Model 20 gas chromatograph equipped with a 200-ft. apiezon "L" capillary column and an argon ionization detector. Although areas were found generally to be proportional to mole percent any deviation from linearity was corrected for by use of calibrated standard samples.

ST. LOUIS, MO.

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(25) Details of the analytical procedure for biphenyl, the three monochlorobiphenyls and the twelve dichlorobiphenyls are reported elsewhere, H. Weingarten *et al.*, *Anal. Chim. Acta, in press.*

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REED COLLEGE]

The Nature of Lagidze's Hydrocarbons. III.[1] The 217° Hydrocarbon Produced by Dehydrogenation of 5,5,10,10-Tetramethyl-4b,5,9b,10-tetrahydroindeno-[2,1,*a*]indene

J. E. H. HANCOCK AND D. L. PAVIA

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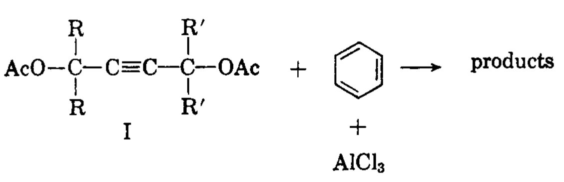
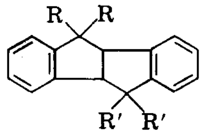
Dehydrogenation of IIa over palladium-on-charcoal at 300–350° yields III.

Previous studies[1–4] in this field have been concerned with the structures of hydrocarbons formed by the following general sequence:

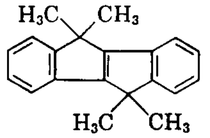


Ia. R = R′ = H
Ib. R = R′ = CH_3
Ic. R = CH_3; R′R′ = $(CH_2)_5$

Recently Lagidze has carried out[4] many different condensations of this type, using both different acetylenic diacetates, and also some substituted benzenes; as a result of this work it would appear that there are in general two types of products—diacetate Ia produces 2-phenylnaphthalene, and all other diacetates apparently give rise to substituted tetrahydroindenoindenes (II).



II



III

IIa. R = R′ = CH_3
IIb. R = CH_3; R′R′ = $(CH_2)_5$

We have studied the mechanisms of these reactions, and it was hoped that Part III of this series would consist of a detailed discussion of the mechanism of formation of 2-phenylnaphthalene; however, no clear-cut evidence in favor of our hypothesis of ring-expansion of indenes[1] has as yet been accumulated, since experiments with these substances have so far only yielded polymeric materials.

It is the purpose of this paper to report on the dehydrogenation of IIa, m.p. 84°. Lagidze has stated[4a] that treatment of IIa with palladium-on-charcoal catalyst at 300° in a carbon dioxide atmosphere gave a hydrocarbon, m.p. 216–217°; he has further claimed that *dehydrogenation of IIb yields the same hydrocarbon.* This interesting report has caused us to examine the dehydrogenation of IIa, but we find it difficult to reconcile our results with the preceding italicized statement, for all the evidence herein presented points to the conclusion that the 217° hydrocarbon has the constitution III. Thus no methane was detected (mass spectrometer) during the dehydrogenation, the infrared absorption

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[1] Part II, J. E. H. Hancock and D. R. Scheuchenpflug, *J. Am. Chem. Soc.*, **80**, 3621 (1958); the title of the series has been changed, since Lagidze's original proposals[2] involving cyclobutadiene-like structures have been withdrawn.[3]

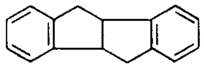
[2] R. M. Lagidze and A. D. Petrov, *Doklady Akad. Nauk, S.S.S.R.*, **83**, 235 (1952).

[3] R. M. Lagidze, N. R. Loladze, and A. D. Petrov, *Soobshchenya Akad. Nauk, Gruzin. S.S.R.*, **19**, 279 (1957); G. Maier, *Chem. Ber.*, **90**, 2949 (1957); J. E. H. Hancock and H. W. Taber, *Tetrahedron*, **3**, 132 (1958); S. W. Fenton *et al.*, *J. Org. Chem.*, **23**, 994 (1958).

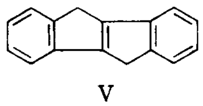
[4] *Cf.*, *inter alia*, (a) R. M. Lagidze and Sh. D. Kuprava, *Doklady Akad. Nauk, S.S.S.R.* **110**, 795 (1956); (b) R. M. Lagidze, N. K. Iremadze, and Sh. D. Kuprava, *Doklady Akad. Nauk, S.S.S.R.*, **121**, 470 (1958); (c) R. M. Lagidze *et al.*, *Soobshchenya Akad. Nauk, Gruzin. S.S.R.*, **25**, 19 (1960).

due to aromatic carbon-hydrogen rocking[5] was affected but little, and catalytic hydrogenation of the 217° hydrocarbon in ethyl acetate over palladium-on-charcoal at room temperature resulted in the uptake of 0.97 mole of hydrogen, and production of IIa. In the NMR spectrum of the 217° hydrocarbon, all the twelve aliphatic hydrogens are equivalent, and the only other hydrogens present are attached to an aromatic ring. (See Experimental.)

Blood and Linstead have reported[6] the dehydrogenation of IV to V over palladized charcoal at 450° (vapor phase); an orange solid was obtained, which could be hydrogenated back to IV.[6,7] These transformations are of immediate relevance to the work reported here, although the orange color of V must have been due to impurities, as both Wawzonek and Brand state[7] that V is colorless; stilbene, an open-chain analog of V, is similarly devoid of color. In our work, the 217° hydrocarbon was accompanied by traces of an impurity which imparted to it a reddish blue fluorescence in daylight, but material which had been chromatographed on alumina did not show this behavior.

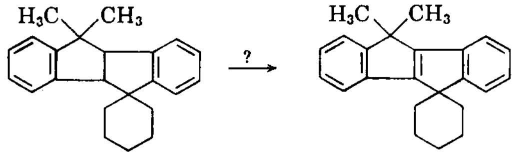


IV



V

In the absence of further data, one is tempted to conclude that dehydrogenation of IIb should yield VI although Lagidze has reported that III is formed instead: this is only one of the surprises in this area, however, as it has also been stated that IIb and IIa yield the same oxidation product, m.p. 204°, on treatment with chromic acid in acetic acid at 100°.[4a]



IIb VI

Studies on these problems are continuing and will be reported in due course.

EXPERIMENTAL

All melting points are uncorrected.

Dehydrogenation of 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1,a]indene (IIa). The above hydrocarbon[1] (2.64 g.) was mixed with 10% palladium-on-charcoal (200 mg.) in a Kjeldahl flask; the apparatus was flushed with nitrogen (purified by passage through alkaline pyrogallol) and the mixture heated at 340–350° for 8 hr. The initial effervescence soon ceased, and the cooled mixture was taken up in chloroform, filtered to remove catalyst, and evaporated to dryness *in vacuo*. The resulting solid crystallized from ethanol containing a little ethyl acetate as plates, m.p. 212.5–214.5° (1.10 g., 42% yield). Unchanged starting material was isolated from the filtrate.

In a prior experiment, designed to duplicate that of Lagidze as much as possible, the reaction was carried out at 300° in a stream of nitrogen, and the exit gases were passed through a spiral tube immersed in liquid nitrogen. After 10 hr. the reaction mixture was allowed to cool, and the trap contents transferred to two evacuated gas sample tubes. Mass spectrometric analysis of these samples (see Acknowledgment) showed presence of nitrogen and traces of water and oxygen, but no methane. The 217° hydrocarbon was isolated in only 18% yield, and most of the remainder was unchanged starting material.

Catalytic hydrogenation of III *to* IIa. A solution of III (260 mg.) in ethyl acetate (30 ml.) was hydrogenated at room temperature and atmospheric pressure, using 10% palladium-on-charcoal catalyst (30 mg.); after 195 min. there was a decrease in the rate of absorption, and 0.97 mole of hydrogen had been absorbed (corrected for absorption by the catalyst). The solution was filtered, evaporated to dryness, and the residue crystallized from approximately 2 ml. of ethanol in a Skau tube, giving 0.18 g. of colorless crystals of IIa, m.p. 82–85°. From the mother liquors an additional 0.03 g. was isolated (m.p. 83–85°) making the total recovery 88%. The infrared spectrum of the first crop (in potassium bromide) was identical with that of the starting material used in the dehydrogenation experiment above.

Infrared spectra. These were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer, and the samples were prepared in a potassium bromide matrix (*ca.* 0.5 mg. in 300 mg. of potassium bromide). The spectrum of the 217° hydrocarbon is much less detailed than that of the starting material. The peaks will be reported in terms of wave length (μ) and per cent transmittance; numbers in bold face signify presence of fine structure.

1 For hydrocarbon IIc. 3.28(38), 3.34(37), 3.42(04), **3.48(07)**, **5.16(80)**, 5.25(69), 5.34(85), 5.44(86), **5.55(83)**, 6.15(72), 6.27(79), 6.34(59), 6.78(05), **6.91(13)**, 7.26(15), 7.34(28), 7.58(55), 7.72(51), 7.79(37), 7.98(71), **8.13(42)**, **8.38(55)**, **8.52(60)**, **8.57(73)**, 8.71(59), **8.87(32)**, **8.97(28)**, 9.25(37), **9.75(35)**, 10.29(87), **10.67(68)**, **11.26(64)**, 11.45(91), 11.56(91), 11.85(91), 12.56(81), **13.28(00)**, **13.43(04)**, 13.60(44), 13.79(86), 13.90(90), 14.20(85), **14.53(57)**.

2 For hydrocarbon III. 3.31(66), **3.41(33)**, 3.46(48), 3.53(58), **4.32(80)** (CO_2?), **5.16(85)**, **5.27(82)**, **5.56(85)**, **6.18(72)**, **6.26(61)**, 6.83(30), 6.89(30), **6.94(42)**, 7.25(61), **7.36(73)**, **7.71(62)**, **7.88(82)**, **8.20(75)**, **8.50(74)**, **8.69(56)**, **8.96(56)**, **9.32(75)**, **9.84(63)**, **10.00(61)**, **10.72(82)**, **12.52(78)**, **13.01(72)**, **13.25(01)**.

Ultraviolet spectra. In 95% ethanol, III showed maxima at 237 (12,000), 245 (10,500), 321 (17,500), and 334 (12,500) mμ, with inflections at 230 (8600), 282 (3200), 298 (8300), and 308 (13,000); for V, Blood and Linstead[6] quote maxima at 237 (6000), 308 (11,000), 315 (13,000), and 328 (8,000).

NMR spectra. Samples were dissolved in carbon tetrachloride, and spectra were obtained using a Varian A-60 spectrometer. The spectrum of IIa was essentially as described in Part II; using tetramethylsilane as standard, IIa gave τ 9.17, 8.55 (methyl groups), 6.20 (benzyl hydrogen), and 2.92 (aromatic ring), and III gave τ 8.53 (methyl groups), 2.87 and 2.80 with some smaller shoulders at 2.93, 2.95, and 2.98 (aromatic ring).

Acknowledgment. We are most grateful to the following people for their kind assistance in this work: Mr. Dean Yeaman and Dr. Alvin Baker (Dow

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(5) *Cf.*, for example, L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, 2nd edition, 1958, p. 65.

(6) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

(7) S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 745 (1940); K. Brand and K. O. Müller, *Ber.*, **55**, 601 (1922).

Chemical Co., Pittsburg, Calif.) performed the mass-spectrometric analyses; Mr. Fred Holling and Mrs. V. Krivoshein (Reed College) have helped us in translation from the Russian; for the NMR spectra we are indebted to Dr. Dietrich Heinert and Mr. Fred Anderson of the Illinois Institute of Technology. We have again exchanged data before publication with Professor R. M. Lagidze, whom we thank for his gracious and continued interest.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (Project No. 324-B).

PORTLAND 2, ORE.

[CONTRIBUTION FROM THE RESEARCH DIVISION, POLAROID CORP.]

Red Dyes of the Azabenzanthrone Series. 1-Substituted 2-Keto-3-alkyl-6-alkylamino-3-azabenzanthrones[1]

MYRON S. SIMON AND JEAN B. ROGERS

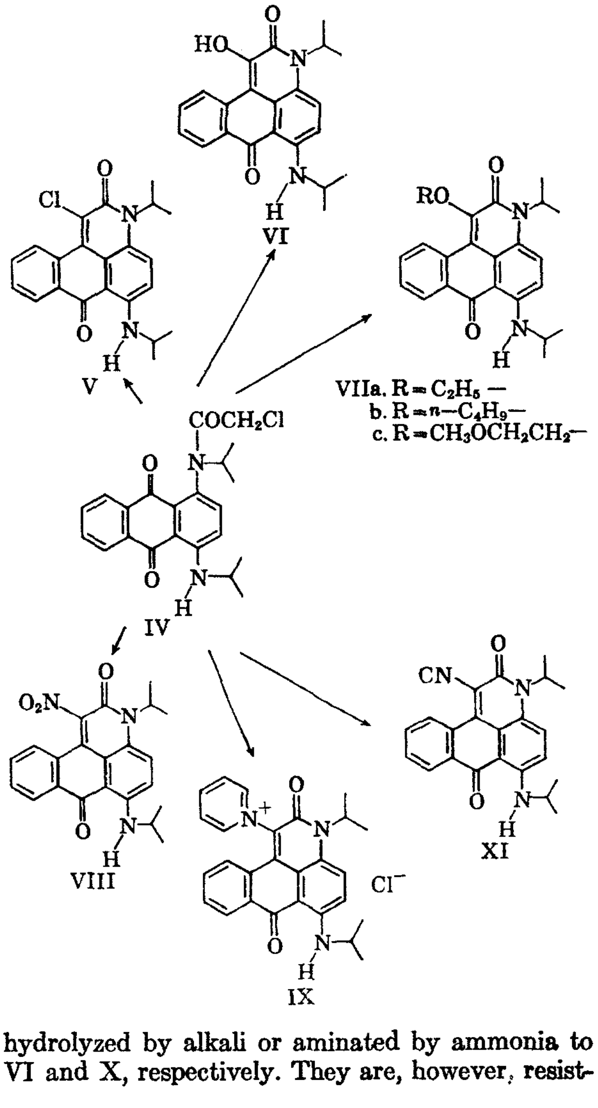
Received April 17, 1961

2-Keto-3-alkyl-6-alkylamino-3-azabenzanthrone dyes containing different substituents in the 1- position were synthesized A correlation between electronegativity of the 1-substituent and position of the visible absorption bands is noted. Several routes to a new type of 2-keto-3-azabenzanthrone dye, the 1-alkoxy derivatives, are reported.

2-Keto-3-azabenzanthrones with amino groups in the 6-position are red dyes. In the fifty years since their discovery the series most studied has been that containing 6-arylamino groups.[2] These have greater stability toward light than the 6-alkylamino dyes, and have an aromatic ring which can be readily sulfonated for water solubility. In an examination of lesser known derivatives of aminoanthraquinones we have made a number of 2-keto-3-azabenzanthrones with alkylamino groups in the 6-position. A few references to such materials appear in the patent literature.[3] We have used the isopropyl group as the representative alkyl group because of the known increase in light stability of alkylaminoanthraquinone dyes when primary alkyl groups on the amine are replaced by secondary alkyl groups.[4]

In the course of this work we have synthesized three members of a type of 2-keto-3-azabenzanthrone dye not previously reported, the 1-alkoxy derivatives. Three routes to their preparation, from *N*-chloracetyl-1,4-bis(*i*-propylamino)anthraquinone (IV), from 1-chloro-2-keto-3-*i*-propyl-6-*i*-propylamino-3-azabenzanthrone (V), and from 1-pyridinium-2-keto-3-*i*-propyl-6-*i*-propylamino-3-azabenzanthrone chloride (IX) were found. The 1-alkoxy dyes have much of the reactivity of simple esters (they are, in fact, vinylogous esters), being hydrolyzed by alkali or aminated by ammonia to VI and X, respectively. They are, however, resist-

Chart I



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[1] These materials are probably best known as anthrapyridones, *e.g.*, "1-substituted 3-alkyl-6-alkylaminoanthrapyridones." *Chemical Abstracts* prefers "1-substituted 3-alkyl-6-alkylamino-7*H*-dibenz[*f,ij*]isoquinoline-2,7[3*H*]-diones," Ring Index No. 5168.

[2] See, *e.g.*, K. Venkataraman, *Synthetic Dyes*, Academic Press, New York, 1952, p. 99; H. A. Lubs, *The Chemistry of Synthetic Dyes and Pigments*, Reinhold, New York, 1955, p. 463.

[3] (a) Bayer, German Patent 201,904 (1907); (b) Sandoz, French Patent 975,917 (1951); (c) E. F. Elslager, U. S. Patent 2,756,234 (1956).

[4] I. G. Farbenindustrie, British Patent 490,372 (1938).