

the diffusion constant  $D_{20}$   $1.09 \times 10^{-7}$ , corresponding to an axial ratio of about 390.

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### THE SYNTHESIS OF CYCLOÏTATETRAENE FROM PSEUDOPELLETIERINE

Sir:

Validity of the synthesis of cycloïtatetraene from the pomegranate bark alkaloid pseudopelletierine by Willstätter, Waser and Heidelberger<sup>1</sup> has been questioned because their product resembled styrene in some physical and chemical properties,<sup>2</sup> and on the basis of studies of model compounds.<sup>3</sup> The synthesis has not been repeated, presumably because pseudopelletierine was not available. Development of a catalytic synthesis of cycloïtatetraene from acetylene in Germany<sup>4</sup> has renewed interest in the hydrocarbon.

We have repeated the Willstätter synthesis of cycloïtatetraene, beginning with synthetic pseudopelletierine,<sup>5</sup> through the following steps. Pseudopelletierine  $\rightarrow$  N-methylgranatoline (82%)  $\rightarrow$  N-methylgranatenine (85%)  $\rightarrow$  methiodide (97%)  $\rightarrow$   $\alpha$ -des-dimethylgranatenine (I) (82%)  $\rightarrow$  methiodide (92%)  $\rightarrow$  cycloïtatriene (II) (70%)  $\rightarrow$  dibromide (not isolated)  $\rightarrow$  bis-(dimethylamino)-cycloïtadiene (III) (47%)  $\rightarrow$  di-methiodide (97.5%)  $\rightarrow$  cycloïtatetraene (7-9%). Physical constants of the intermediates corresponded closely to those reported originally.<sup>1</sup> Ultraviolet absorption spectra were consistent with conjugated diene structures for I and III, and a conjugated triene structure for II ( $\lambda_{\max}$  2650 Å.,  $\log \epsilon$  3.57).

The cycloïtatetraene which was obtained gave a satisfactory analysis (calcd. for  $C_8H_8$ : C, 92.26; H, 7.74. Found: C, 92.47; H, 7.91), and had the following properties: m. p. (capillary)  $-5.8$  to  $-5.4^\circ$ ;  $n_D^{25}$  1.5342; m. p. (hot stage) of the

(1) Willstätter and Waser, *Ber.*, **44**, 3423 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

(2) Noted by Vincent, Thompson and Smith, *J. Org. Chem.*, **3**, 603 (1939). Also, dehydrogenation of cycloïtene yields styrene; Goldwasser and Taylor, *THIS JOURNAL*, **61**, 1260 (1939).

(3) Hurd and Drake, *ibid.*, **61**, 1943 (1939). Investigation of other models led to a different conclusion: Hurd and Ensor, paper presented before the Division of Organic Chemistry at the Chicago Meeting of the American Chemical Society, September, 1946 (Abstracts, page 24M). For a review see Baker, *J. Chem. Soc.*, 258 (1945).

(4) Reported in "German Synthetic Fiber Developments," p. 631 (translation of an article by W. J. Reppe), Textile Research Institute, New York, N. Y., 1946 (PB. 7416) and other Department of Commerce reports.

(5) Prepared by modifications of the small-scale synthesis of Schöpf and Lehmann, *Ann.*, **518**, 1 (1935).

(6) Ref. 1 reports m. p.  $-27^\circ$ . Other physical properties are in fair agreement.

maleic anhydride adduct  $166.7-168.2^\circ$ ; per cent. hydrogen absorbed in catalytic hydrogenation over platinum 101.5%. The m. p. of the cycloïtatetraene and its maleic anhydride adduct were not depressed by mixture with a sample prepared from acetylene and its corresponding derivative, respectively. Cycloïtatetraene from the two sources had identical ultraviolet absorption spectra, and showed no important differences in infrared absorption spectra.<sup>7</sup>

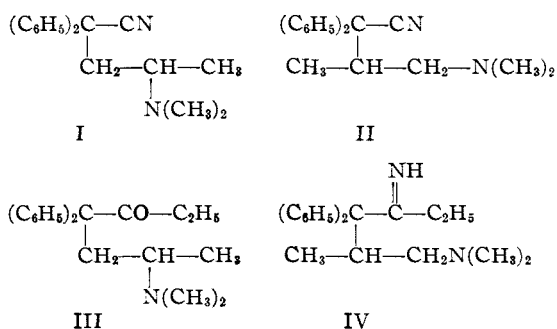
(7) We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared data.

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### SOME ISOMERS OF AMIDONE AND RELATED COMPOUNDS

Sir:

It has recently been shown that the reaction between diphenylacetonitrile and 1-dimethylamino-2-chloropropane results in a mixture from which two isomeric aminonitriles (I and II) have been isolated.<sup>1</sup> The higher melting nitrile (I) reacts with ethylmagnesium bromide to yield Amidone (III). We have now found that the lower melting nitrile (II) reacts with ethylmagnesium bromide to give a ketimine (IV) which was isolated as the sesquioxalate (m. p.  $145-146^\circ$ . *Anal.* Calcd. for  $2C_{21}H_{28}N_2 \cdot 3H_2C_2O_4$ : C, 64.99; H, 7.05; N, 6.32;  $H_2C_2O_4$ , 30.45. Found: C, 65.15; H, 6.96; N, 6.36;  $H_2C_2O_4$ , 30.50). This was also characterized as the dihydrochloride (m. p.  $200-202^\circ$  dec. *Anal.* Calcd. for  $C_{21}H_{28}N_2 \cdot 2HCl$ : C, 66.13; H, 7.93; N, 7.35; Cl, 18.59. Found: C, 66.00; H, 7.75; N, 7.30; Cl, 18.43) and the dipicrate (m. p.  $140-141^\circ$ . *Anal.* Calcd. for  $C_{21}H_{28}N_2 \cdot 2C_6H_5O_7N_3$ : C, 51.69; H, 4.47; N, 14.62. Found: C 51.65, 51.75; H, 4.54, 4.38; N, 14.41, 14.58).



This ketimine was found to be remarkably resistant to hydrolysis, being only partially converted to the ketone (Isoamidone II, V) by boiling for five hours with an excess of 20% hydrochloric

(1) E. M. Schultz, C. M. Robb and J. M. Sprague, *THIS JOURNAL*, **69**, 188 (1947).