azo compound[7] has been reported, with ultraviolet absorption maximum and rate of decomposition quite similar to those of the acyclic analogs,[1] the size of the ring apparently allowing the azo linkages to assume the *trans* configuration. Decomposition of 0.036 mole/l. of I in 3.46 moles/l. styrene in ethylbenzene at 80° led to polymerization of 8.5 molecules of styrene per molecule of I.

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[7] C. Overberger and M. Lapkin, THIS JOURNAL, **77**, 4651 (1955).

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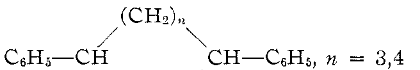
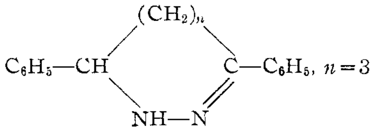
SEVEN- AND EIGHT-MEMBERED RING AZO COMPOUNDS

Sir:

We wish to report the synthesis and decomposition of the azo compounds (I)



Decomposition of these cyclic azo compounds should provide biradicals of the benzyl type. The preparation of the six-membered ring analog is also described in this issue.[1] A method for the preparation of the hydrazine precursor of I, $n = 3$, by reduction of the azine with lithium aluminum hydride has been reported previously.[2] As a preparative method, this procedure is unsatisfactory owing to the formation of the hydrazone (II)



λ_{max} 290 mμ, log ϵ 3.73, from incomplete reduction of the azine and from isomerization of the azo compound obtained by autoxidation of the hydrazine under the conditions of isolation. Quantitative reduction of the cyclic azine[2] with hydrogen over 10% palladium-on-charcoal followed by immediate oxidation of the crude hydrazine with mercuric oxide gives 29.4% of I, $n = 3$, m.p. 115°, with gas evolution, λ_{max} 290 mμ, log ϵ 2.21, λ_{max} 389 mμ, log ϵ 2.03. *Anal.* Calcd. for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.51; H, 7.01; N, 11.23. Air oxidation of the crude hydrazine has also yielded the azo compound. The normal azo absorption found in acyclic azo compounds at approximately 350 mμ,[3] has been displaced to 389 mμ, presumably due to the *cis* configuration forced on the azo link in I, $n = 3$. Thermal decomposition of I, $n = 3$, in xylene solution at 100.2° gives first-order kinetics, half-life 2.9 minutes, with a 94% evolution of nitrogen after 31 minutes. Decomposition of I in xylene at 80° gave a half-life of 27.1 minutes with only a 71.5% evolution of nitrogen. These decomposition rates are over 100 times faster than the corresponding linear *trans*[3] azo compounds. Analysis of products of the decomposition at 80° indicates the presence of the hydrazone II, $n = 3$, λ_{max} 290 mμ, log ϵ 3.60. Analysis of the ultraviolet spectrum of I, $n = 3$, has shown that I slowly isomerizes to the hydrazone II, $n = 3$, in ethanol at room temperature.

The synthesis of the eight-membered ring azo compound I, $n = 4$, was carried out by preparing the appropriate cyclic azine by a modification of the method of Overberger and Lapkin,[4] m.p. 136–137°, λ_{max} 268 mμ, log ϵ 4.45. *Anal.* Calcd. for $C_{18}H_{18}N_2$: C, 82.42; H, 6.92; N, 10.68; mol. wt., 262. Found: C, 82.64; H, 6.90; N, 10.43; mol. wt. 281 (ebullioscopic in butanol). Quantitative reduction of the azine followed by immediate oxidation with mercuric oxide yielded 57% of I, $n = 4$, m.p. 88–90°, λ_{max} 368 mμ, log ϵ 1.65. *Anal.* Calcd. for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63; N, 10.60; mol. wt., 264. Found: C, 81.60; H, 7.47; N, 10.73; mol. wt., 297 (ebullioscopic in butanol).[5] The infrared absorption for both I, $n = 3,4$, are almost identical, show no hydrazone absorptions and confirm the conclusions made from ultraviolet data.

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[1] C. H. Wang, S. Hsiao, E. Saklad and S. G. Cohen, THIS JOURNAL, **79**, 2661 (1957).

[2] C. G. Overberger and J. J. Monagle, *ibid.*, **78**, 4470 (1956).

[3] S. G. Cohen, S. J. Groszos and D. B. Sparrow, *ibid.*, **72**, 3947 (1950).

[4] C. G. Overberger and M. Lapkin, *ibid.*, **77**, 4651 (1955).

[5] J. M. Zanden and G. DeVries, *Rec. trav. chim.*, **75**, 1159 (1956) have reported the preparation of the 3,8-di-(*p*-anisyl) derivative of I, $n = 4$.

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