m.p. 123–124°, $[\alpha]^{21}D$ +76° (*c* 0.91, $CHCl_3$). *Anal.* Calcd. for $C_{15}H_{23}O_9N$: C, 49.86; H, 6.42. Found: C, 49.71; H, 6.45. Catalytic deacetylation of III with barium methylate afforded methyl 2-acetamido-2-deoxy-α-D-gulopyranoside (yield 72%) (IV), m.p. 79–82°, $[\alpha]^{25}D$ +72° (*c* 0.74, CH_3OH). *Anal.* Calcd. for $C_9H_{17}O_6N$: C, 45.95; H, 7.29. Found: C, 45.80; H, 7.22. A crystalline *O*-benzylidene derivative was prepared, m.p. 111–114°, $[\alpha]^{25}D$ +71° (*c* 0.90, CH_3OH). *Anal.* Calcd. for $C_{16}H_{21}O_6N$: C, 59.43; H, 6.55. Found: C, 59.08; H, 7.07. 2-Amino-2-deoxy-D-gulose hydrochloride (D-gulosamine hydrochloride) (V) was obtained in a 66% yield by treatment of IV with hydrochloric acid, 150–170° dec., $[\alpha]^{22}D$ +6.1° (10 min.) → −17.9° (36 hr.) (*c* 0.90, H_2O). *Anal.* Calcd. for $C_6H_{14}O_5NCl$: C, 33.26; H, 6.48; N, 6.50; Cl, 16.44. Found: C, 33.47; H, 6.56; N, 6.32; Cl, 16.52. A crystalline derivative was prepared, 2-deoxy-2-(2′-hydroxynaphthylidenamino)-D-gulose, m.p. 186–188° dec., $[\alpha]^{22}_{5461}$ − 150° (at equilibrium, *c* 0.60, methyl cellosolve). *Anal.* Calcd. for $C_{17}H_{19}O_6N$: C, 61.26; H, 5.75. Found: C, 61.16; H, 5.86. The structure of V was ascertained by degradation with ninhydrin in presence of pyridine[4] to D-xylose, identified by paper chromatography. Chromatographed on paper in the mixture *n*-propanol–ammonia 1% 70:30, V migrated 1.18, compared to D-glucosamine 1.00, D-galactosamine 0.91, and D-allosamine[5] 1.03. Treatment of V with pyridine and acetic anhydride, followed by reflux with methanolic hydrochloric acid and subsequent reacetylation of the crude product with pyridine and acetic anhydride, gave a compound, m.p. 116–119°, $[\alpha]^{23}D$ −54° ($CHCl_3$) to which the structure of a methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-gulopyranoside (VI) was attributed on the basis of the sequence of reactions, rotation and analysis, Found: C, 49.69; H, 6.58.

A sample of natural gulosamine,[6] chromatographed on paper had the same R_f value as V. Submitted to the above described treatment, it gave a compound, m.p. 116–119°, $[\alpha]^{23}D$ −53°, showing no depression of the m.p. in admixture with VI.

(4) P. J. Stoffyn and R. W. Jeanloz, *Arch. Biochem. Biophys.*, **52**, 373 (1954).

(5) R. W. Jeanloz, THIS JOURNAL, **79**, 2591 (1957).

(6) We are very grateful to Dr. John R. Dyer, Georgia Institute of Technology, Atlanta, Georgia, for providing a sample of natural D-gulosamine hydrochloride.

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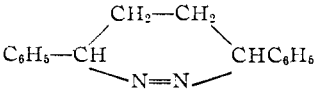
RECEIVED FEBRUARY 21, 1957

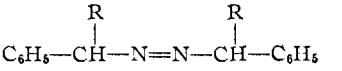
A CYCLIC AZO COMPOUND, 3,6-DIPHENYL-3,4,5,6-TETRAHYDROPYRIDAZINE (I)

Sir:

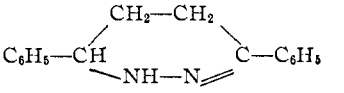
We wish to report the preparation and decomposition of the six-membered cyclic azo compound (I)



a potential source of the biradical 1,4-diphenyl-1,4-butadiyl (II) $C_6H_5\dot{C}HCH_2CCH_2HC_6H_5$ which is of interest as possibly being formed by interaction of two molecules of styrene monomer during thermal polymerization. Compound I is analogous to the acyclic azo compounds[1] (III) R = CH_3 or



C_2H_5, which lead to styrene-type radicals. Attempts to prepare a six-membered cyclic azo compound analogous to azo-bis-iso-butyronitrile[2] failed, apparently because of thermal instability. A previously reported[3] synthesis of I had in fact led to the hydrazone-type tautomer[4] (IV)



λ_{max} 292 mμ, log ε 4.19.

Compound I was prepared by (1) addition of diethyl azo-dicarboxylate to 1,4-diphenylbutadiene-1,3, forming the adduct, 1,2-dicarboethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine, 95% yield, m.p. 134–136°, reported[5] 132°; (2) hydrogenation of the adduct to the hexahydro derivative, 70% yield, m.p. 85–87°, reported[5] 87°; (3) saponification with potassium hydroxide and decarboxylation in boiling methanol under nitrogen, and autoxidation during concentration of the dried ether extract, 22% yield, decomposing with vigorous gas evolution when placed in a bath at 120°, λ_{max} 287 mμ, log ε 3.49, λ_{max} 387 mμ, log ε 2.89. *Anal.* Calcd. for $C_{16}H_{16}N_2$: C, 81.30; H, 6.82; N, 11.85. Found: C, 81.48; H, 6.92; N, 11.75. The absorption due to the azo linkage is displaced from its normal position at about 350 to 387 mμ, apparently because of the *cis* configuration of I, acyclic aliphatic azo compounds normally having the *trans* configuration about the azo-linkage. Compound I is tautomerized readily to IV, by heat or by polar solvents.

Thermal decomposition of I in dilute solution in decalin at 135 and 100°, in ethylbenzene at 100°, and in 3.46 moles/l. styrene in ethylbenzene at 100° and at 80° leads to essentially quantitative evolution of nitrogen. Thermal decomposition of solid I leads to partial isomerization to IV; styrene is formed as one of the products of decomposition of solid I, identified as the dibromide, m.p. and mixed m.p. 68–70°, reported[6] 72–73°. The decomposition in solution at 80° had a half-life of about 20 minutes and appeared about 100 times as fast as that of the acyclic analog[1] III, due apparently to the *cis* nature of the cyclic compound and possibly in part due to concomitant formation of the styrene. A large (24-membered) ring bis-

(1) S. G. Cohen, S. J. Groszos and D. B. Sparrow, THIS JOURNAL, **72**, 3947 (1950).

(2) C. G. Overberger, N. R. Byrd and R. R. Mesrobian, *ibid.*, **78**, 1961 (1956).

(3) A. P. J. Hoogeveen and C. V. van Hoogstraten, *Rec. trav. chim.*, **52**, 378 (1933).

(4) S. G. Cohen and C. H. Wang, THIS JOURNAL, **77**, 2457 (1955).

(5) K. Alder and H. Niklas, *Ann.*, **585**, 81 (1954).

(6) R. Fittig and E. Erdmann, *ibid.*, **216**, 194 (1883).

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.

Acknowledgment.—We are pleased to acknowledge generous support of this work by the National Science Foundation (NSFG575).

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

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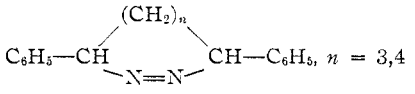
RECEIVED FEBRUARY 12, 1957

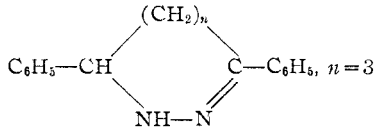
SEVEN- AND EIGHT-MEMBERED RING AZO COMPOUNDS

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.

Acknowledgment.—We wish to thank the National Science Foundation for the support of a portion of this work, Grant NSF-1453.

(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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