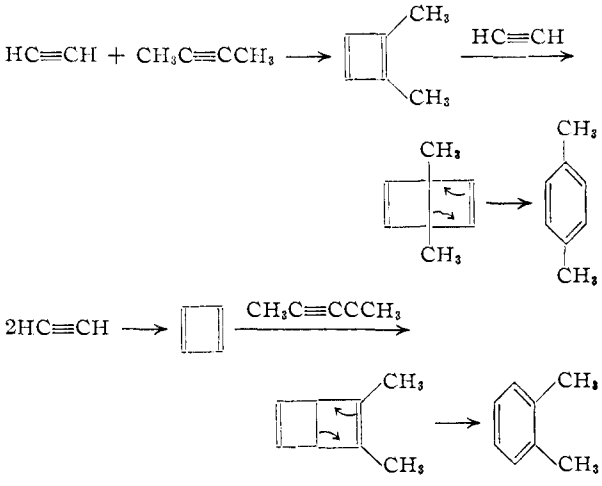
This reaction sequence necessitates having the terminal methylene group of the heptatrienenitrile derived from the acrylonitrile rather than from the acetylene. A tracer study was carried out to test this hypothesis.

For this purpose, C^{14}-labeled 2,4,6-heptatrienenitrile was prepared by the reaction of labeled acrylonitrile ($\overset{*}{C}H_2=\overset{*}{C}H$-CN) with acetylene in the presence of a nickel carbonyl/triphenylphosphine catalyst. The terminal methylene group in the heptatrienenitrile was then removed by ozonolysis and found to contain virtually no C^{14}. This result affords strong evidence that the terminal methylene group in heptatrienenitrile is derived from acetylene and not from acrylonitrile. Accordingly, it appears that heptatrienenitrile is not formed by a cyclobutadiene mechanism. Similar results were obtained in parallel experiments with labeled methyl 2,4,6-heptatrienoate prepared from acetylene and labeled methyl acrylate.

Another extension of the cyclobutadiene mechanism would suggest that some *p*-xylene, as well as *o*-xylene, should be formed in the cotrimerization of dimethylacetylene with acetylene.



We were, however, unable to detect any *p*-xylene by ultraviolet or infrared analyses.

The labeled acrylonitrile (rel. molar activity 3.8 × 10^5 dis./min.) was prepared by pyrolysis of labeled lactonitrile acetate at 555–560°. The acetate was made by heating labeled vinyl acetate, hydrogen cyanide and potassium cyanide catalyst.[3] Labeled 2,4,6-heptatrienenitrile (rel. molar activity 3.9 × 10^5 dis./min.) was prepared by injecting acetylene into the labeled acrylonitrile.[2] The heptatrienenitrile was ozonized in methylene chloride by the procedure of Clemo and Macdonald.[4] The crude formaldehyde containing other ozonolysis products was converted into the dinitrophenylhydrazone (m.p. 151–158° after recrystallization from methanol (0.19 g., 13%), rel. molar activity 0.4 × 10^5, or a drop in activity of 89.7%). The dinitrophenylhydrazone recovered from the mother liquor (0.14 g., 10%) had a relative molar activity of 0.3 × 10^5, or a drop in activity of 92.3%. The derivative appeared to be essentially pure dinitrophenylhydrazone of formaldehyde based on infrared analysis.

Tagged methyl heptatrienoate (rel. molar activity 60 × 10^4 dis./min.) was prepared from tagged methyl acrylate and acetylene.[2] Ozonolysis gave formaldehyde whose dinitrophenylhydrazone showed a drop in relative molar activity of 98%.

In the dimethylacetylene/acetylene cotrimerization, the reactants were heated with a $Ni(CO)_2/[C_6H_5)_3P]_2$ catalyst in tetrahydrofuran at 80–165° under a bomb gage pressure of 5–15 atm. for 3 hr. Benzene, styrene and *o*-xylene were identified as products. There was no indication of the presence of even small amounts of *p*-xylene (based largely on infrared and ultraviolet spectral data).

CONTRIBUTION NO. 416
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RECEIVED APRIL 4, 1957

(3) E. L. Carpenter, British Patent 591,489 (1947).

(4) G. R. Clemo and J. McL. Macdonald, *J. Chem. Soc.*, 1294 (1935).

THE SYNTHESIS OF D-GULOSAMINE

Sir:

A new aminosugar has been isolated recently from streptothricin and streptolin B and the structure of a 2-aminosugar, D-gulosamine, has been proposed for it.[1] This appears to be the first reported isolation of a naturally occurring 2-aminohexose other than the well known D-glucosamine and D-galactosamine. It is also the first isolation of a naturally occurring sugar with the gulose configuration.

We wish to report the synthesis of a 2-aminohexose, possessing the D-gulosamine configuration and also having identical properties to the naturally isolated compound described above. Methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside[2] treated with methanesulfonyl chloride in pyridine solution gave an 86% yield of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methylsulfonyl-α-D-galactopyranoside (I), m.p. 219–220°, $[\alpha]^{24}D$ +169° (*c* 1.12, $CHCl_3$). *Anal.* Calcd. for $C_{17}H_{23}O_8NS$: C, 50.86; H, 5.77; S, 7.99. Found: C, 50.93; H, 5.86; S, 7.90. Hydrolysis of I with 60% acetic acid afforded a quantitative yield of methyl 2-acetamido-2-deoxy-3-*O*-methylsulfonyl-α-D-galactopyranoside (II), m.p. 179–180°, $[\alpha]^{22}D$ +132° (*c* 0.88, CH_3OH). *Anal.* Calcd. for $C_{10}H_{19}O_8NS$: C, 38.33; H, 6.11. Found: C, 38.48; H, 6.22. It was characterized by the 4,6-di-*O*-acetyl derivative, m.p. 163–164°, $[\alpha]^{24}D$ +96° (*c* 0.83, $CHCl_3$). *Anal.* Calcd. for $C_{14}H_{23}O_{10}NS$: C, 42.31; H, 5.83. Found: C, 42.22; H, 5.79. A solution of II in methyl cellosolve heated in the presence of sodium acetate[3] gave a product, subsequently acetylated with pyridine and acetic anhydride. After purification by chromatography, a 56% yield of methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-gulopyranoside (III) was obtained;

(1) E. E. Van Tamelen, J. R. Dyer, H. E. Carter, J. V. Pierce and E. E. Daniels, THIS JOURNAL, **78**, 4817 (1956).

(2) P. J. Stoffyn and R. W. Jeanloz, *ibid.*, **76**, 561 (1954).

(3) B. R. Baker, R. E. Schaub, J. P. Joseph and J. H. Williams, *ibid.*, **76**, 4044 (1954).

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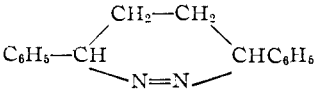
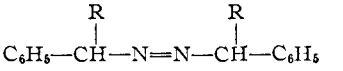
A CYCLIC AZO COMPOUND, 3,6-DIPHENYL-3,4,5,6-TETRAHYDROPYRIDAZINE (I)

Sir:

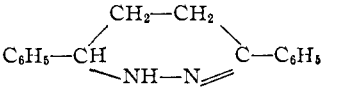
We wish to report the preparation and decomposition of the six-membered cyclic azo compound (I)



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-

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(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).