hydrolyzed into uridine in 3 hr,[3,5,7] and at pH 8.55 in 0.2 *M* ammonium chloride solution a rapid conversion of this product into cytidine took place[3,5,7] and was complete in 30 min, the half-time of the ammonolysis being 4 min, a period identical with that observed when an authentic sample of uridine-4-sulfonate[3] was subjected to the identical treatment. When these acid- or ammonia-treated samples were paper chromatographed (solvent 2[6]), a single spot of uridine or cytidine, respectively, was detectable on the chromatogram. Recovery, as estimated by extracting the spot with 0.01 *N* hydrochloric acid, was 0.88 μmole for uridine and 0.83 μmole for cytidine, starting from 1 μmole of 4-thiouridine. Considering technical losses during the work-up, the transformation of 4-thiouridine into uridine or cytidine under the above conditions appeared to be quantitative. Only speculative guesses could be made at this stage of research regarding the mechanism of this new reaction.

We found that 4-thiouridine forms a reversible complex with HSO_3^- ions. This complex formation was observable by the instantaneous decrease in the characteristic absorption at 330 mμ of 4-thiouridine, when the nucleoside was dissolved in sodium hydrosulfite solution in the nitrogen atmosphere. The complex formation was more pronounced in solutions of higher HSO_3^- concentrations,[8] and it was most extensive at pH values lower than 5. A hypothetical structure is presented in Scheme I for this complex. Structure II is analogous to that of bisulfite adducts of carbonyl compounds.[9] The reaction, 4-thiouridine $\leftrightarrow$ complex II, was found to be reversible with respect to the change in concentrations of HSO_3^- ions.

We speculate that this complex formation is the first step of the over-all reaction. By some mechanism which is to be investigated, complex II is transformed into uridine-4-sulfonate. In this transformation, oxygen and, possibly, sulfite ions as well would be participating. In this regard it is noteworthy that 4-thiouridine was inert to molecular oxygen in the absence of sodium sulfite (see Figure 1).

A peculiar feature of the reaction is that the high concentration of sodium sulfite inhibits the over-all reaction. This also awaits explanation by future work.

Acknowledgments. The author is grateful to Mr. M. Yano of our laboratory for his technical assistance and to Professor T. Ukita for his hearty encouragement throughout this research.

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[7] M. Yano and H. Hayatsu, manuscript in preparation.

[8] For example, in 1 *M* sodium hydrosulfite solution at pH 4, 4-thiouridine gave an A_{330} value 15% of that obtainable in water.

[9] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 441–442.

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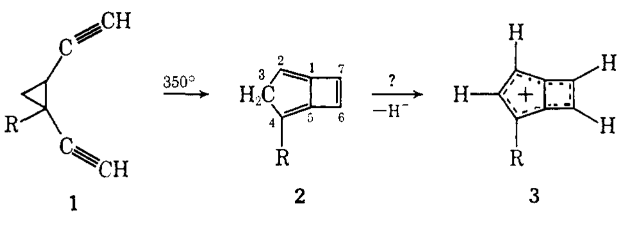
Thermal Conversion of 1-Methyl-1,2-diethynylcyclopropane to 2-Methylbicyclo[3.2.0]hepta-1,4,6-triene

Sir:

We report the synthesis and isolation of 2-methylbicyclo[3.2.0]hepta-1,4,6-triene (**2**, R = CH_3). This material is formed on flow pyrolysis of 1-methyl-1,2-diethynylcyclopropane (**1**, R = CH_3) in a nitrogen stream at 350° and is of interest due to its possible high degree of strain and potential use as a precursor[1] of cyclically conjugated[2] bicycloheptatrienyl systems (*e.g.*, **3**). The facility of the **1** → **2** rearrangement[3] and the remarkable stability of triene **2** prompt us to communicate our preliminary observations at this time.



Direct irradiation of diazopropyne[4] (λ >3000 nm) in diethyl ether solution in the presence of 2-methyl-but-1-en-3-yne[5] is complete in 20 min. Analytical vapor chromatographic (vpc) analysis of the concentrated solution reveals the presence of two new hydrocarbons in the ratio 2:1. The minor product decomposes upon preparative vapor chromatography of the mixture, but the major isomer[6] can be collected (*ca.* 20% yield based on diazopropyne) and shown to have gross structure **1** (R = CH_3) by virtue of its pmr, ir, and mass spectra (pmr: τ 8.18 (1 H, doublet, J = 2 Hz), 8.23 (1 H, singlet), 8.30 (1 H, multiplet), 8.58 (3 H, singlet), 8.73 (1 H, doublet of doublets, J = 7, 4 Hz), and 9.25 (1 H, triplet, J = 4 Hz); ir: 3300, 3080, 3010, 2125, 1440, 1385, 1250, 945, and 930 cm^{-1}; mass spectrum: principal peaks (70 eV) at 104, 103, and 78).

Pyrolysis of **1** (R = CH_3) at 350° in a flow apparatus (nitrogen carrier gas) gives rise to a single product (30–40% yield) which exhibits significant absorption in the ultraviolet [λ_{max} 204 (ϵ 1.4 $\times$ 10^4), 277 nm (ϵ 2.1 $\times$ 10^3)]. Its mass spectrum shows that it is an isomer of starting material (parent peak at *m/e* 104), but the material exhibits no acetylenic carbon–carbon or carbon–hydrogen absorption in the ir. It can be purified by preparative vpc (6 ft $\times$ 0.25 in. 20% SE-30 on Chromosorb P, 100°); that its structure is indeed **2** (R = CH_3) is confirmed by the pmr, which exhibits signals for the cyclobutene hydrogens at τ 3.21 (1 H) and 3.33 (1 H), the one additional vinyl hydrogen at τ 4.97 (1 H), the allylic methylene at τ 6.72 (2 H), and the methyl group at τ

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[1] (a) R. Breslow, W. Washburn, and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969); (b) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *ibid.*, **91**, 2787 (1969); (c) M. P. Cava, K. Narasimham, W. Zieger, L. J. Radonovich, and M. D. Glick, *ibid.*, **91**, 2379 (1969).

[2] (a) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965; (b) J. O. Halford, *J. Am. Chem. Soc.*, **89**, 5338 (1967).

[3] There is precedent in acyclic systems for this rearrangement; *cf.* W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **89**, 342 (1967).

[4] (a) P. S. Skell and J. Klebe, *ibid.*, **82**, 247 (1960); (b) J. V. Gramas, Ph.D. Dissertation, Pennsylvania State University, 1965; (c) diazopropyne was routinely generated and used in solution. In neat form, it decomposes explosively.

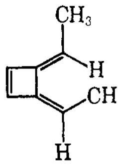
[5] Aldrich Chemical Co.

[6] We believe that isolated diyne **1** has both acetylenic functions *trans*, and that the unstable minor product of the irradiation is the corresponding *cis* isomer. We are attempting to isolate *cis*-**1** in order to compare its thermal reactivity with *trans*-**1** and the closely related *cis*-divinylcyclopropane.[7]

[7] W. von E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963).

8.22 (3 H).[8] This compares very favorably with the spectrum of a model bismethylenecyclobutene **4**, which shows[3] pmr absorption at τ 3.13, 3.30, 4.74, 5.02, 8.21, and 8.27.

Triene **2** is a colorless oil which solidifies at −78°. Although it reacts rapidly with oxygen and polymerizes at a moderate rate in neat form, nmr concentrations of **2** ($\sim$0.5 *M*) are stable for several days at 0° under an inert atmosphere. This contrasts with the fact that both its double-bond isomer **5** and the corresponding benzo derivative **6** dimerize immediately upon generation in solution.[1a-c]



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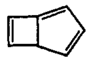

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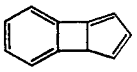
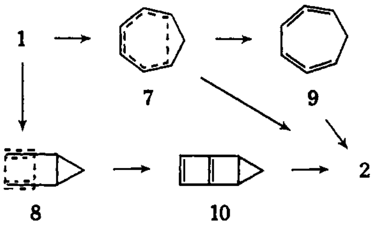


6

The most reasonable first bond-formation transition state for the **1** → **2** isomerization appears to be either **7** or **8**. These species differ primarily in their extent of 1,5 bonding; both appear to be highly strained. Whether any of the diastereomers of cyclic bisallene **9** or fused cyclobutadiene **10** constitute minima on the energy surface leading to **2** remains conjectural.



Efforts are now under way aimed at converting **2** to spectrally observable concentrations of a number of fully conjugated bicycloheptatrienyl systems, and at applying the **1** → **2** reaction type in the synthesis of heterocyclic compounds isolectronic with these derivatives.

Acknowledgments. We are grateful to the Frederick Gardner Cottrell Fund of the Research Corporation and the Arthur A. Noyes Fund for partial support of this work.

[8] All couplings in the molecule are small and there seems to be some long-range coupling, resulting in broadening of the vinyl proton lines. The methyl group appears to be a four-line pattern due to coupling with the methylene hydrogens ($J \cong$ 0.5–1.0 Hz) and one of the cyclobutene hydrogens ($J \cong$ 0.5–1.0 Hz). The methylene hydrogens appear to be coupled to the 5-ring vinyl proton ($J \cong$ 2 Hz) as well as to the methyl group.

[9] National Defense Education Act Predoctoral Trainee, 1967–present.

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The Reactions of Tellurium Atoms. I

Sir:

The atomic reactions of the group VIa elements oxygen,[1,2] sulfur,[3] and selenium[4-7] have been extensively studied, but little work has been done on the reactions of tellurium atoms. Tellurium atoms and tellurium alkyls have been known to be antiknocks for some time. Callear and Norrish[8] detected the presence of Te atoms in investigations of the antiknock properties of dimethyl telluride; however, no investigation of the atomic reactions was made. In recent flash photolysis studies we found that the uv photolysis of dimethyl telluride (DMT) is a usable source of $^3P_{2,1,0}$ tellurium atoms.

The uv absorption spectrum of DMT indicates two major systems, one with a maximum at 2500 Å, the other at 2000 Å. The absorption at shorter wavelengths shows considerable structure while that at longer wavelengths displays additional maxima at 2425 and 2575 Å. With the quartz reaction vessels used, absorption took place in both systems.

In flashed mixtures of DMT vapor (10^{-3}–10^{-1} Torr with CO_2 diluent) using kinetic absorption spectroscopy, we observed intense atomic absorptions at λ 2143 and 2259 Å corresponding to known transitions of Te($^3P_2$) and at 2386 and 2383 Å corresponding to Te ($^3P_1$) and ($^3P_0$), respectively. Several molecular systems were also observed. One appearing between 3600 and 4300 Å corresponds to that assigned to the Σ–Σ type transition of the Te_2 molecule;[9] another, a regular progression of eight bands between 2750 and 2850 Å, has not yet been assigned. At low initial pressures of DMT, the 2160-Å absorption of the CH_3 radical was detected.

From flash energy variations, the carrier of a series of four bands between 2240 and 2430 Å appears to be a primary photoproduct, very likely the CH_3Te radical. The appearance of another system in the same region follows the decay of CH_3Te closely. More precise kinetic studies are being undertaken in an attempt to clarify the orgin of these systems.

In the presence of added ethylene two further band systems have been observed. The system between 2400 and 2500 Å (band heads at 2472, 2410, and possibly at 2356 Å) has a lifetime of several milliseconds and has been assigned to the unstable ethylene epitelluride molecule. The other system around 2300 Å decays faster ($\sim$250 μsec) in an apparent first-order process. Analogous spectra (at 2480 and 2458 Å) have also been obtained with added propylene.

The formation of transient epitelluride molecules has been confirmed by kinetic mass spectrometry. The flash photolysis–kinetic mass spectrometry apparatus has been described in earlier communications.[10,11] Flashing 0.2 Torr of DMT in the presence of 10 Torr of propylene, the parent adduct C_3H_6Te (*m/e* 172) has been detected. At this mass number there was no inter-

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[1] F. Kauffman, *Progr. Reaction Kinetics*, 1, 1 (1961).

[2] R. J. Cvetanović, *Advan. Photochem.*, 1, 115 (1963).

[3] H. E. Gunning and O. P. Strausz, *ibid.*, 4, 143 (1966).

[4] A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, 61, 2395 (1965).

[5] A. B. Callear and W. J. R. Tyerman, *ibid.*, 62, 371 (1966).

[6] A. B. Callear and W. J. R. Tyerman, *ibid.*, 62, 2760 (1966).

[7] W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 4277 (1966).

[8] A. B. Callear and R. G. W. Norrish, *Proc. Roy. Soc.*, **A259**, 304 (1960).

[9] B. L. Jha and D. Ramchandra Rao, *Chem. Phys. Letters*, 3, 175 (1969).

[10] O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Am. Chem. Soc.*, 89, 4805 (1967).

[11] W. J. R. Tyerman, M. Kato, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).