by its infrared spectrum which was identical with the spectrum of known sulfur dioxide.[14]

The sulfone was recrystallized from ether to give white crystals, m.p. 75–78°. Further recrystallizations gave material melting at 82–84°. The substance crystallized with 0.5 mole of ether which was not removed completely even on pumping at 0.05-mm. pressure with gentle heating. The ether was detected by a proton n.m.r. spectrum of the episulfone. A typical ether spectrum was observed in deuterioacetone in addition to complex multiplets centered at 425 and 445 c.p.s. (relative to tetramethylsilane at 60 Mc.). The relative areas of the absorption peaks for the aromatic protons *vs.* the ether protons were 20:5 corresponding to the empirical formula $C_{28}H_{20}O_4S \cdot 0.5C_4H_{10}O$. The areas under the two absorptions for the methylene protons in the ether were in the ratio of 6:4.

Anal. Calcd. for $C_{28}H_{20}O_4S \cdot 0.5C_4H_{10}O$: C, 73.59; H, 5.15; S, 6.55; mol. wt. (assume dissociation), 326. Found: C, 73.45; H, 5.26; S, 6.66; mol. wt., 339, 348 (boiling point elevation in acetone).

The molecular weight of a sample (m.p. 128–129°) recrystallized from water–acetic acid, in which the etherate did not form, was determined from the elevation of the boiling point of ethylene dichloride.

Anal. Calcd. for $C_{28}H_{20}O_4S$: C, 74.31; H, 4.48; S, 7.09; mol. wt., 453. Found: C, 74.83; H, 4.80; S, 6.79; mol. wt., 428, 426, 453.

The ultraviolet spectrum had no defined maxima, λ (dioxane) 260 and 235 mμ.

Acknowledgment.—We wish to thank Dr. W. A. Sheppard and Dr. E. A. LaLancette for helpful discussion.

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[14] "Sadtler Standard Spectra," Midget Edition, The Sadtler Research Laboratories, Philadelphia, Pa., 1962, No. 841.

Notes

Preparation of 1,2,3-Triazoles from 7-Azido-1,3,5-cycloheptatriene. A Displacement from Nitrogen

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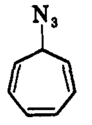
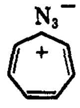
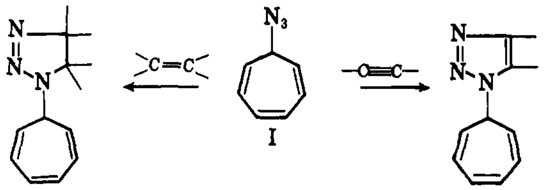
Tropylium azide (7-azido-1,3,5-cycloheptatriene) has been prepared previously,[1] and its n.m.r. spectrum shows that it has the covalent structure I. The ionic form II may exist in ionizing solvents.[2] The covalent structure is also suggested by its physical state (liquid); ionic cycloheptatrienylium compounds are high-melting solids. The observation that no solid separated from a mixture of methyl tropyl ether and hydrazoic acid in ether further supports this assignment since separation of ionic tropylium bromide occurred when hydrogen bromide was passed into a solution of ditropyl ether.[3]

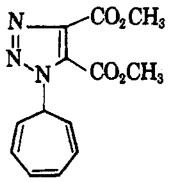

I

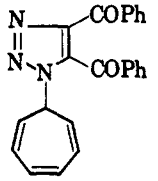

II

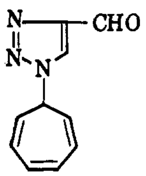
Phenyl and benzyl azide can be added to a variety of acetylenes and olefins to produce triazoles and triazolines, respectively.[4–6] Tropylium azide, with the covalent structure I, should undergo addition in a similar manner to form adducts with the seven-membered ring attached to nitrogen.



Addition of the azide I to acetylenes did occur when an electron-attracting group was attached to the triple bond. Dimethyl acetylene dicarboxylate, dibenzoylacetylene, and propargyl aldehyde condensed smoothly and gave triazoles III, IV, and V, respectively. Diacetylacetylene afforded only tar under the same conditions. Without a strong electron-withdrawing group present on the triple bond (phenylacetylene or diphenylacetylene), addition did not occur.


III


IV


V

Two attempts were made to prepare triazolines from tropylium azide. 1,4-Naphthoquinone was recovered unchanged when heated with azide I. Maleic anhydride gave an unresolvable mixture which may have resulted from a competing Diels–Alder addition of the dienophile to the cycloheptatriene ring.

The structures of adducts III, IV, and V are supported by their n.m.r. spectra. Each spectrum has a triplet, representing one proton, between τ 5.2 and 5.4 which is due to the proton at position 7 of the 1,3,5-cycloheptatriene ring. The remaining bands in each spectrum also agree with the proposed structures. The formyl group in structure V was assigned to the 4-

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[1] C. E. Wulfman, C. J. Yarnell, and D. S. Wulfman, *Chem. Ind.* (London), 1440 (1960).

[2] D. S. Wulfman, L. Durham, and C. E. Wulfman, *ibid.*, 859 (1962).

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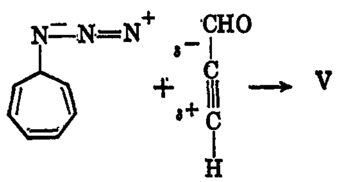
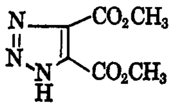
[5] F. Moulin, *Helv. Chim. Acta*, **35**, 167 (1952).

[6] W. Kirmse and L. Horner, *Ann.*, **614**, 1 (1958).

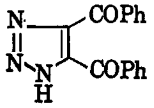


position on the basis of the polarization of the reactants and the mechanism of dipolar addition.[7]

The ability of the cycloheptatrienyl group to leave a carbon, nitrogen, or oxygen atom has been established.[8] The adducts III, IV, and V would be expected to undergo a similar displacement in acid. When compounds III and IV were treated with hydrogen chloride in ether, tropylium chloride separated and triazoles VI and VII were isolated from the respective solutions.



VI



VII

Cleavage probably occurred by protonation of the substituted nitrogen atom, with subsequent loss of the organic cation. Triazole V did not give a cleavage product under these conditions.

Experimental

7-Azido-1,3,5-cycloheptatriene[1] (I).—A solution of 7.1 g. (0.040 mole) of tropylium tetrafluoroborate in 60 ml. of water was stirred while a solution of 3.0 g. (0.046 mole) of sodium azide in 10 ml. of water was added dropwise. An oil separated which was extracted into benzene or methylene chloride. The extract was washed with water, dried, concentrated, and distilled immediately, b.p. 36–40° (0.1 mm.). Redistillation gave 3.0 g. (56%), b.p. 70–72° (7 mm.), $n^{25}D$ 1.5461 [lit.[1] b.p. 50° (1 mm.), $n^{25}D$ 1.5466]. The infrared spectrum showed the presence of the azide group at 2120 cm.$^{-1}$. On standing at 25°, a solid separated and the liquid became black. The azide could be stored for short periods (24 hr.) at −10° under nitrogen.

When methyl tropyl ether[3] was allowed to stand overnight in an ether solution of excess hydrazoic acid, no solid separated.

1-(2,4,6-Cycloheptatrienyl)-4,5-dicarbomethoxy-1,2,3-triazole (III).—A solution of 1.7 g. (0.013 mole) of freshly distilled tropylium azide and 1.8 g. (0.013 mole) of dimethyl acetylenedicarboxylate in 10 ml. of carbon tetrachloride was heated carefully on a steam bath until the initial evolution of heat stopped. After an additional 30 min. of heating at reflux, the solvent was removed and the residue was recrystallized from ligroin–ether; yield 2.6 g., 73%, m.p. 63–64°.

Anal. Calcd. for $C_{13}H_{13}N_3O_4$: C, 56.7; H, 4.8; N, 15.3. Found: C, 56.5; H, 4.7; N, 15.2.

The product was obtained in 64% yield (7.0 g.) when undistilled tropylium azide, from 7.1 g. (0.040 mole) of tropylium tetrafluoroborate and 3.0 g. (0.046 mole) of sodium azide, was heated for 2 hr. with 5.6 g. (0.040 mole) of dimethyl acetylenedicarboxylate in 60 ml. of carbon tetrachloride.

4,5-Dicarbomethoxy-1,2,3-triazole[9] (VI).—A solution of 3.5 g. (0.013 mole) of 1-(2,4,6-cycloheptatrienyl)-4,5-dicarbomethoxy-1,2,3-triazole (III) in 100 ml. of ether was treated with hydrogen chloride for 1 hr. and the tropylium chloride which separated was collected; yield, 1.7 g. (100%). The filtrate was washed with water, dried, concentrated, and recrystallized from benzene to give 0.8 g. (34%), m.p. 129–130° (lit.[9] m.p. 133°).

Anal. Calcd. for $C_6H_7N_3O_4$: C, 39.0; H, 3.8; N, 22.7. Found: C, 39.1; H, 3.9; N, 23.0.

1-(2,4,6-Cycloheptatrienyl)-4,5-dibenzoyl-1,2,3-triazole (IV).—Tropylium azide was prepared from 2.0 g. (0.031 mole) of sodium azide and 5.0 g. (0.028 mole) of tropylium tetrafluoroborate and extracted into 50 ml. of benzene. After drying, 3.5 g. (0.015 mole) of dibenzoylacetylene was added and the mixture was heated for 2 hr. on a steam bath. Removal of the solvent and recrystallization of the residue from ethanol gave 3.2 g. (58%), m.p. 75–77°.

Anal. Calcd. for $C_{23}H_{17}N_3O_2$: C, 75.2; H, 4.7; N, 11.4. Found: C, 74.9; H, 4.5; N, 11.4.

4,5-Dibenzoyl-1,2,3-triazole (VII).—Hydrogen chloride was passed through a solution of 1.0 g. (0.0027 mole) of 1-(2,4,6-cycloheptatrienyl)-4,5-dibenzoyl-1,2,3-triazole (IV) in 100 ml. of ether for 30 min. and the residue was collected (0.34 g., 100%, tropylium chloride). The filtrate was concentrated, washed with water, and dried to give 0.75 g. (100%) of the triazole VII, m.p. 164–165°. This compound has been previously reported but with no mention of the preparation or the melting point.[10]

The triazole VII was also obtained in 13% yield by allowing 2.3 g. of dibenzoylacetylene to stand for 2 days at room temperature with an excess of hydrazoic acid in benzene–ether. The product melted at 164–165° after recrystallization from ethanol and did not depress the melting point of material obtained from IV.

Anal. Calcd. for $C_{16}H_{11}N_3O_2$: C, 69.3; H, 4.0; N, 15.2. Found: C, 69.0; H, 4.0; N, 15.3.

1-(2,4,6-Cycloheptatrienyl)-4-formyl-1,2,3-triazole (V).—Tropylium azide was prepared from 6.0 g. (0.092 mole) of sodium azide and 14.0 g. (0.080 mole) of tropylium tetrafluoroborate and extracted into methylene chloride. The organic extract was dried, concentrated, and taken up in a solution of 4.3 g. (0.089 mole) of propargyl aldehyde in 50 ml. of carbon tetrachloride. The solution was heated on a steam bath for 2 hr. and concentrated, and the residue was distilled to give 10.0 g. (67%) of product, b.p. 92–94° (0.07 mm.), $n^{25}D$ 1.5750.

Anal. Calcd. for $C_{10}H_9N_3O$: C, 64.1; H, 4.9; N, 22.4; mol. wt., 187. Found: C, 64.2; H, 4.9; N, 22.2; mol. wt., 187 (mass spectra).

Attempted Preparation of 4-Formyl-1,2,3-triazole.—Hydrogen chloride was passed through a solution of 5.0 g. of 1-(2,4,6-cycloheptatrienyl)-4-formyl-1,2,3-triazole (V) in 100 ml. of ether for 30 min. The solid was collected and the filtrate was washed with water, dried, and concentrated. A small amount of unidentifiable oil remained.

Attempted Condensation of Diphenylacetylene and Phenylacetylene with Tropylium Azide.—A solution of 6.7 g. (0.050 mole) of tropylium azide and 8 g. (0.045 mole) of diphenylacetylene in benzene was heated at reflux for 3 days. Removal of the solvent and distillation of the residue gave 7.5 g. (94%) of unchanged diphenylacetylene. When toluene was used as a solvent and the reaction time was 24 hr., 70% of the starting material was recovered unchanged.

Phenylacetylene and tropylium azide (0.02 mole of each) were heated in benzene at reflux for 2 hr. Upon distillation, 64% of the azide was recovered. No higher-boiling material remained in the flask.

Acknowledgment.—The author wishes to express his thanks to Miss Thelma J. Davis, Mr. David P. Maier, and Dr. J. Kenneth O'Loane for discussions concerning infrared, mass, and n.m.r. spectra, respectively.

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17-Azasteroids. III.[1] The Synthesis of N-Hydroxy-17a-aza-D-homosteroids

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Recent publications[2–4] from this laboratory described the synthesis of various 17-azasteroids. It was of

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(1) This work was supported, in part, by a National Institutes of Health Grant H-5266.

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(4) S. Rakhit and M. Gut, *Steroids*, **4**, 291 (1964).