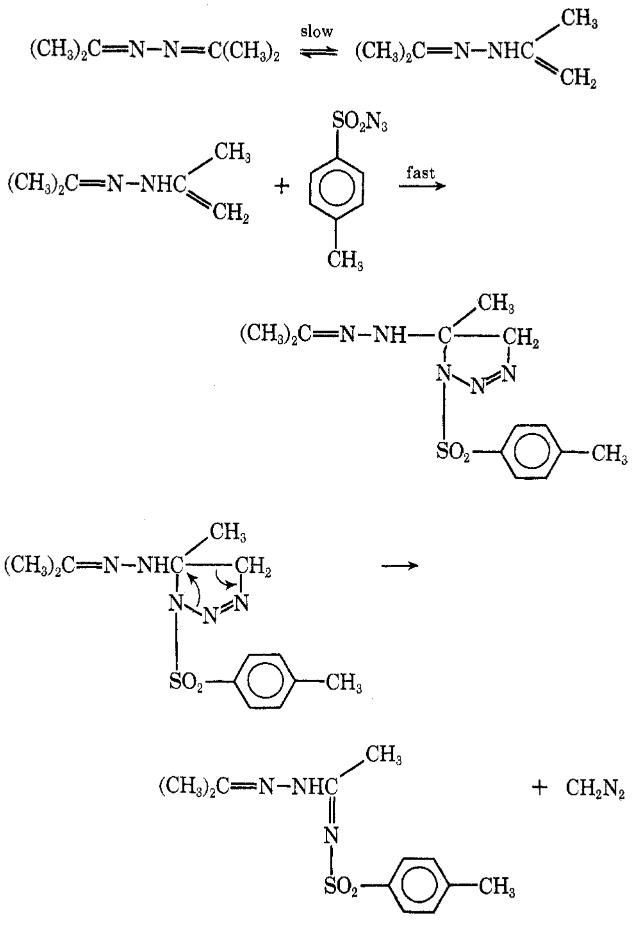
yield of **1** was obtained after 7 days. The reaction occurred at approximately the same rate at which deuterium (from D_2O) was incorporated into the azine. The structure of **1** was confirmed by the nmr spectrum which showed the absorptions of four different methyl groups, the infrared spectrum which showed the absorption of the NH group, and the ultraviolet absorption spectrum.

Scheme I is suggested for the reaction. The slow incorporation of deuterium into acetone azine is in agreement with the postulated equilibrium between the azine and the substituted hydrazone. The hydrazone would be expected to undergo rapid deuterium exchange and thus provide a means for the entrance of deuterium into the azine. The azide should add rapidly to the enamine derivative to give the triazoline.[1,2] Analogous fragmentations of triazolines to diazo compounds have been observed previously.[1-3] Diazomethane was not isolated from the reaction but suggestive evidence for its formation was obtained by the isolation of methyl *p*-nitrobenzoate from the reaction of acetone azine, *p*-toluenesulfonyl azide, and *p*-nitrobenzoic acid.

SCHEME I



1

Experimental Section

N-[1-(Isopropylidenehydrazino)ethylidene]-*p*-toluenesulfonamide (1).—A solution of 12 g of acetone azine and 20 g of *p*-toluenesulfonyl azide in 50 ml of tetrahydrofuran was heated at reflux for 7 days. Gas was slowly evolved. The mixture was cooled and the solvent was removed under reduced pressure. The residue was stirred with methanol and filtered to give white, crystalline **1**, 3.19 g (12%), mp 154–156.5°. Recrystallization from methanol gave material which melted at 158–159°: uv λ_{max}^{EtOH} 264 mμ (ϵ 23,400), 224 (13,100); nmr ($CDCl_3$) δ 1.98 (3), 2.05 (3), 2.22 (3), 2.42 (3), 7.58 (4).

Anal. Calcd for $C_{12}H_{17}O_2N_3S$: C, 53.91; H, 6.41; N, 15.72; S, 11.99; mol wt, 267. Found: C, 53.62, 53.75; H, 6.38, 6.48; N, 15.57, 15.45; S, 11.90, 11.80; mol wt (mass spectrum), 267.

From the original methanol filtrate there was obtained in successive crops a total of 6.18 g (36%) of *p*-toluenesulfonamide, mp 125–126° from benzene.

Acetone Azine in Deuterium Oxide.—A solution of acetone azine in deuterium oxide was heated at 65°. After 4 days the intensity ratio of the two azine methyl groups to the exchange peak of H_2O in D_2O in the nuclear magnetic resonance spectrum was 6.3, indicating exchange of 14% of the original methyl hydrogens for deuterium. After 9 days the ratio was 4.6 (18% exchange) and after 16 days the ratio was 3.2 (24% exchange).

Registry No.—**1**, 31600-81-4; acetone azine, 627-70-3; *p*-toluenesulfonyl azide, 941-55-9.

Acknowledgment.—We wish to thank Dr. Howard E. Simmons for helpful discussions

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[1] R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963).

[2] J. Kuvera and Z. Arnold, *Tetrahedron Lett.*, 1109 (1966).

[3] M. Regitz and F. Menz, *Chem. Ber.*, **101**, 2622 (1968).

On the Structure of the Diels-Alder Adduct of Ditropyl and Dimethyl Acetylenedicarboxylate

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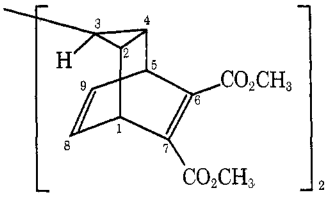
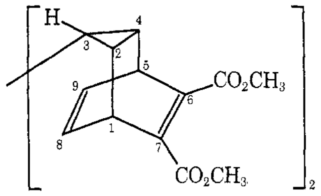
Recently we assigned structure I to the Diels-Alder adduct of ditropyl and 2 mol of dimethyl acetylenedicarboxylate,[1] by employing both nmr evidence and reactivity arguments. However, the configuration at C-3 (and C-3′) could not be unequivocally established. Thus, the nmr signal at τ 9.08 which we confidently assign to the hydrogen at C-3 (and C-3′) moves upfield to τ 9.49 when all of the double bonds are hydrogenated. Since, in the most likely anti-3-exo arrangement[2] Ia,



1a



1b

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[1] G. H. Wahl, Jr., and K. Weiss, *J. Org. Chem.*, **35**, 3902 (1970).

[2] M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4417 (1965).

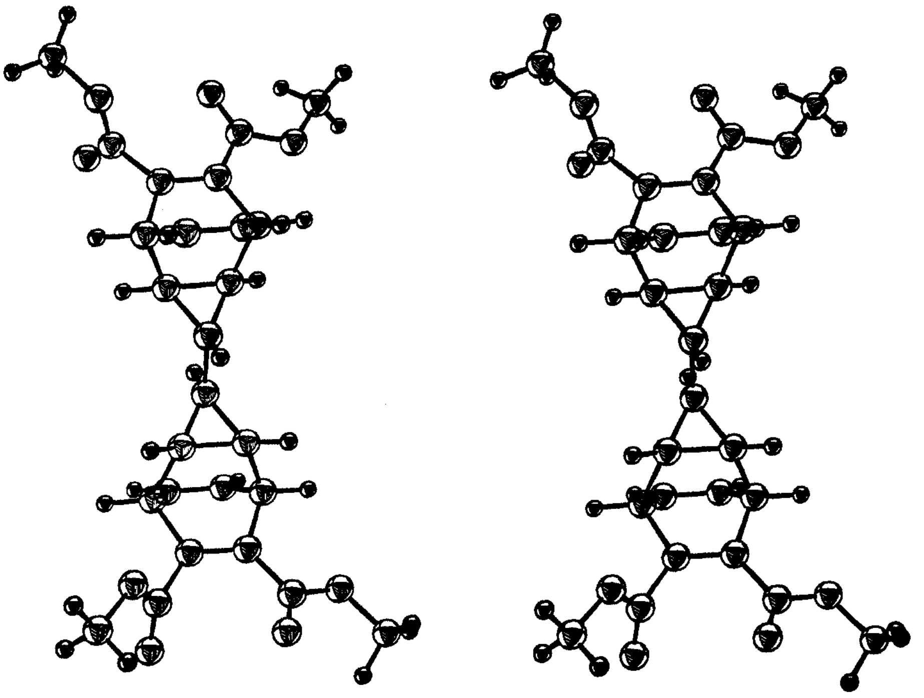

Figure 1.—ORTEP stereoscopic view of tetramethyl (3,3′-bitricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene)-6,6′,7,7′-tetracarboxylate (Ia).

H-3 is held rigidly in the π cloud of the proximate double bond, it might be expected that this arrangement would confer extra shielding on this hydrogen.[3] Furthermore, after hydrogenation, which removes this feature, the resonance should shift downfield. Since the reverse effect is found,[1] the anti-3-endo configuration Ib in which H-3 (and H-3′) would not be expected to experience as large a shielding effect from the adjacent double bond must be considered.

The structure of the Diels–Alder adduct was unambiguously established as Ia (see Figure 1) by a routine, single crystal X-ray analysis. Intensity data (1 Å) (maximum sin θ/λ = 0.5) was collected on a Syntex $P\bar{1}$ diffractometer using copper radiation.[4] Phasing was accomplished using a reiterative application of Sayre's equation.[5,6] A trial structure was obtained with the first E map, and this trial structure refined smoothly to a final R index of 0.068. The final cycle of full matrix least-squares refinement contained the scale factor, coordinates, and anisotropic temperature factors for all the nonhydrogen atoms.[7] The hydrogen positions were located using difference Fourier techniques. While the hydrogen parameters were included in the structure factor calculations, they were not subjected to refinement. Crystal and data collection parameters are presented in Table I. All bond distances and angles were normal and are not presented here. Full details of the X-ray analysis can be obtained from one of the authors (J. B.).

TABLE I

CRYSTAL AND DATA COLLECTION PARAMETERS

Crystallization medium, methanol
Cell dimensions, a = 6.312 Å, b = 11.89 Å, c = 30.59 Å, β = 97.88 Å
Scan mode, $\theta/2\theta$
Scan rate, 2°/min in 2θ
Background count time, 0.5 (scan time)
Density calcd, 1.362 g/cc
Density obsd, 1.32 g/cc
Space group, $P2_1/c$ (4 molecules/unit cell)

This unequivocal assignment of structure and the results of other studies[2,8] permit the conclusion that the three-membered ring which is generated in most Diels–Alder reactions of cycloheptariene and its 7-substituted derivatives will usually be situated in an anti geometry with respect to the dieneophile. Moreover, the predominant or exclusive epimer formed from 7-substituted cycloheptatrienes will possess the anti-3-exo configuration. Finally, the above-mentioned nmr arguments[3] for assigning stereochemistry should be used with extreme caution.[9]

Registry No.—Ia, 31528-84-4.

Acknowledgments.—Partial support of this work from the North Carolina State University Engineering Foundation and Faculty Research and Professional Development Fund is acknowledged with pleasure. We are grateful to Professor Karl Weiss for helpful discussion of this manuscript.

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(3) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 231.

(4) Monochromatic radiation was obtained by use of a graphite monochromator.

(5) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

(6) The phasing process was facilitated by the use of a computer program written by R. E. Long, UCLA. Of the 16 possible solutions generated by the program, the one which converged in the fewest number of cycles (seven) and had the highest internal consistency index (0.69372) proved to be correct.

(7) Of the 2355 reflections collected, 1937 reflections had F's greater than twice their standard deviation. These 1937 reflections were used in the least-squares refinement. Refinement was terminated when the calculated shifts were one-tenth the standard deviation for the positional parameters.

(8) G. H. Wahl, Jr., *J. Org. Chem.*, **33**, 2158 (1968).

(9) Y. E. Rhodes, P. E. Schueler, and V. G. DiFate, *Tetrahedron Lett.*, 2073 (1970). These authors present nmr data on related model systems which suggest that the distant double bond deshields H-3 about as effectively as the closer π system shields it.