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cis- and trans-BICYCLO[6.1.0]NONAN-2, 3 and 4 ONES (1)

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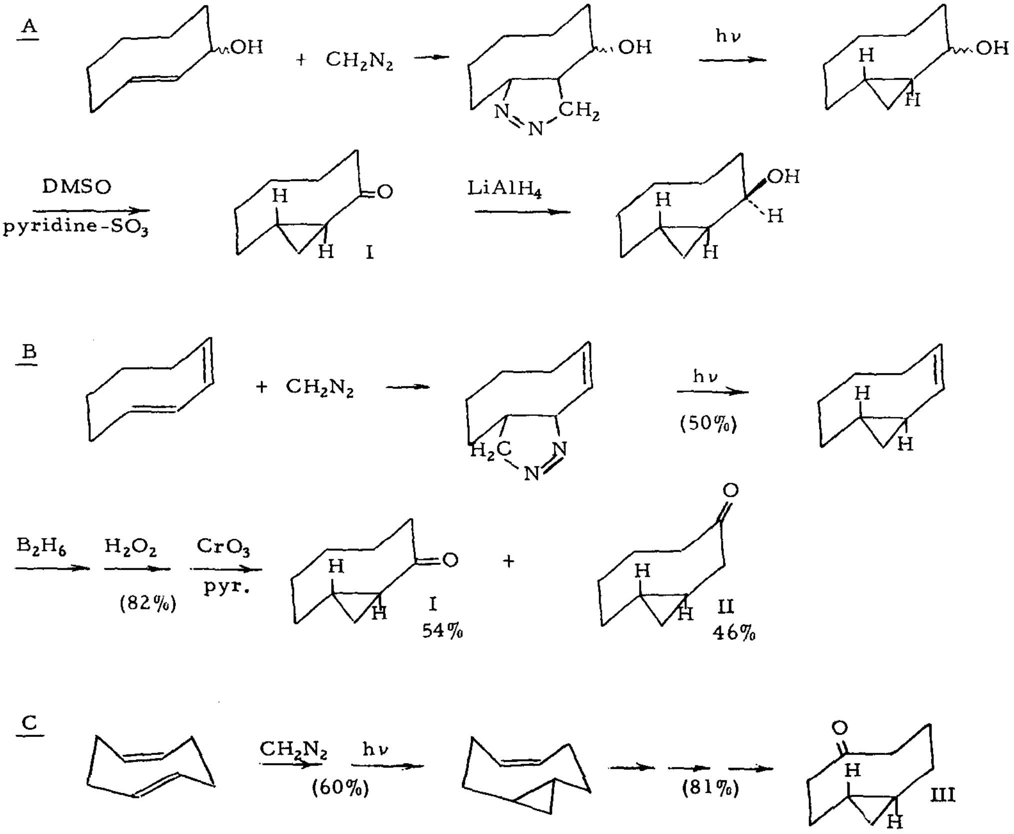
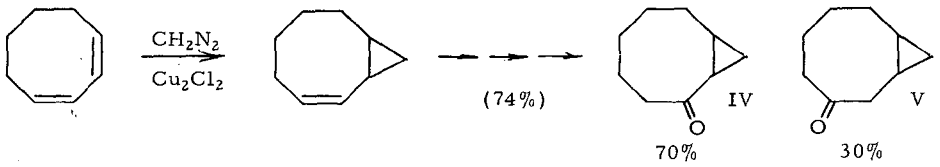
Bicyclic compounds containing trans-fused cyclopropane rings are of interest both with regard to bond angle deformation effects and the effect of trans fusion on the conformation of the larger ring. We wish to report the synthesis of the set of cis and trans-fused bicyclo-[6.1.0]nonanones (2) and to give preliminary data concerning their ultraviolet spectra.

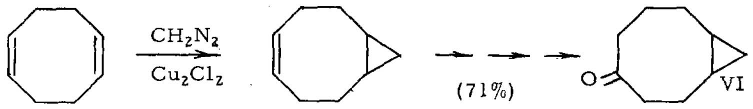
The synthetic routes are outlined below:



D



E



Sequence *A* utilizes the *trans*-cyclooct-1-en-3-ol described by Whitham and Wright (3) and is similar to that used by DePuy and Marshall (2). The addition of diazomethane to the *trans*-double bond proceeded rapidly, and the photolysis of the pyrazoline also proceeded well. It was interesting to note that lithium aluminum hydride reduction of I gave the indicated epimer in at least 90% purity as indicated by nmr and vpc. In sequence *B* the addition of diazomethane to *cis*, *trans*-1, 3-cyclooctadiene (4) occurred only at the *trans*-double bond (5), and subsequent photolysis gave 50% of *trans*-bicyclo[6. 1. 0]non-2-ene. Hydroboration and oxidation gave I and II in approximately equal ratio. A similar set of reactions starting with *cis*, *trans*-1, 5-cyclooctadiene (6) gave *trans*-bicyclo[6. 1. 0]nonan-4-one (III).

The *cis*-fused ketones could be prepared from the *cis*, *cis*-dienes as shown in sequence D and E. Here, the cyclopropane ring could easily be introduced using the cuprous halide catalyzed addition of diazomethane (7).

On treatment with sodium methoxide in anhydrous ether, I was converted to the *cis*-fused isomer, IV. The reaction could be followed by vpc and had a half-life of about 8 hrs at room temperature. When IV was treated with sodium methoxide under the same conditions, 0. 3% of I was found in the recovered ketone. If the entropies of I and IV are assumed to be about the same, the ratio of ketones corresponds to a difference in enthalpy of 3. 5 kcal/mole which is considerably less than the difference between *cis*- and *trans*-cyclooctene (9 kcal/mole) (8).

In the nmr spectra of the *cis*-fused 3 and 4-ketones (V, VI), the *endo*-proton of the cyclopropyl methylene group absorbs at considerably higher field than the *exo*-proton (9). The carbonyl group in the *cis*-2 ketone (IV) appears to shift the *endo*-proton downfield. With all the *trans*-fused ketones, the cyclopropane methylene protons have similar chemical shifts. We have found this to apply to *trans*-bicyclo[6.1.0]nonane and to a number of other derivatives of this ring system. Models of the *trans*-fused compounds suggest that the cyclopropane methylene protons should have similar environments.

The ultraviolet spectra of the ketones are summarized in Table I, along with the infrared carbonyl stretching frequencies. The 4-substituted ketones appear to be quite normal. The 2-ketones lead to increased band intensities for the $n \rightarrow \pi^*$ transition. However, whereas the *cis*-2-ketone exhibits a small red shift, the *trans*-ketone shows a larger blue shift. Both 3-ketones show a red shift and an increased band intensity for the $n \rightarrow \pi^*$ transition. It appears that there is a significant interaction between the cyclopropane ring and the carbonyl group for the 3-ketones as well as the 2-ketones.

The $n \rightarrow \sigma^*$ transition could be observed only for two of the ketones; the others gave end absorption. A detailed analysis of the interaction in these ketones will be postponed until the vacuum ultraviolet spectra are obtained.

TABLE I

Spectral Data for Bicyclo[6.1.0]nonanones

Ketone	UV (acetonitrile)				UV (hexane)		IR
	$n \rightarrow \sigma^*$ (10)		$n \rightarrow \pi^*$		$n \rightarrow \pi^*$		
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	$\nu_{C=O}$ (cm^{-1})
cis-2	198.8	2860	289.0	41	293.0	36	1693
cis-3	< 188		293.7	43	298.0	34	1700
cis-4	< 188		286.2	14	288.0	14	1710
trans-2	192.3	4900	282.0	67	286.0	51	1704
trans-3	< 188		293.0	38	296.0	28	1699
trans-4	< 188		288.5	14	289.0	14	1704

References

(1) This investigation was supported by the U.S. Army Research Office, Durham.

(2) The bicyclo[6.1.0]nonan-2-ones have been reported by C.H. DePuy and J.L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968).

(3) G.H. Whitham and M. Wright, *Chem. Comm.*, 294 (1967).

(4) R.S. Liu, *J. Am. Chem. Soc.*, **89**, 112 (1967).

(5) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1960).

(6) A.C. Cope, C.F. Howell, J. Bowers, R.C. Lord and G.M. Whitesides, *J. Am. Chem. Soc.*, **89**, 4024 (1967).

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

(8) R.B. Turner and W.R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).

(9) This is generally observed with the cis-fused bicyclo[n.1.0]alkanes and their derivatives: W.G. Dauben and W.T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).

(10) This band has frequently been assigned to the $\pi\rightarrow\pi^*$ transition (cf. E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958)), but has been shown to be the $n\rightarrow\sigma^*$ transition (H. Prugger and F. Dörr, Z. Elektrochem., 64, 425 (1960), cf. S. Feinleib and F.A. Bovey, *Chem. Comm.*, 978 (1968).