

residue was crystallized from methanol to give 1.25 g. of material, m.p. 193–195.5° (reported¹⁸ m.p. 194°).

5 α -Pregnan-3,20-dione.—5 α -Pregnan-3 β -ol-20-one, 1.1 g., was dissolved in 50 ml. of acetone (previously distilled from potassium permanganate) and 1.5 ml. of Jones reagent (8 N in H₂SO₄:H₂O) was added dropwise over a 15-minute period. The mixture was allowed to stand at room temperature 1.0 hr. Water was added and the solid was removed by filtration. The solid was crystallized from methanol and gave 890 mg. of plates, m.p. 202–202.5° (reported¹⁷ m.p. 200.5°).

Δ^2 -22 α ,25 α ,5 α -Spirostene was prepared by synthesizing tigogenin tosylate and then eliminating the tosyl group by heating in γ -collidine. Crystallization of the product from methanol yielded needles, m.p. 183–185° (reported¹⁸ m.p. 182–184°).

22 α ,25 α ,5 α -Spirostane was prepared by hydrogenation of 2.3 g. of Δ^2 -22 α ,25 α ,5 α spirostene in 50 ml. of ethanol with 100 mg. of 10% palladium-on-carbon. The solution was filtered and the solvent was removed. The residue was crystallized from methanol and gave 2.2 g. of plates, m.p. 175–178° (reported¹⁸ m.p. 173–175°).

5 α -Pregnane-20-one.— Δ^2 -22 α ,25 α ,5 α -Spirostane, 2.2 g., was heated in a sealed tube with 6 ml. of acetic anhydride for 4 hours. After cooling, the mixture was poured into a flask and 4 ml. of water was added. The mixture was warmed slightly to decompose the excess acetic anhydride. Acetic acid, 25 ml., was added and the mixture was cooled to 10°. A solution of 750 mg. of chromium trioxide in 5 ml. 80% acetic acid was added slowly over a 20-min. period. The mixture was allowed to stir at room temperature for 1.5 hours and was poured into water and extracted with chloroform. The chloroform was washed well with water, sodium bicarbonate solution, water and then was dried. After removal of the solvent a waxy solid was obtained. This solid was dissolved in 50 ml. of ethyl acetate with 200 mg. of palladium-on-barium sulfate catalyst and subjected to atmospheric hydrogenation. The theoretical amount of hydrogen was taken up in 15 minutes. The solution was filtered, the solvent was removed and the residue was crystallized from methanol to give 1.3 g. of colorless needles, m.p. 115–115.5° (reported¹⁹ m.p. 115°).

(16) W. Taylor, *Biochem. J.*, **60**, 380 (1955); **62**, 332 (1956).

(17) S. Lieberman, K. Dobringer, B. R. Hill, L. F. Fieser and C. P. Rhoads, *J. Biol. Chem.*, **172**, 263 (1948).

(18) J. Pataki, G. Rosenkranz and C. Djerassi, *J. Am. Chem. Soc.*, **73**, 5375 (1951).

TABLE I
DIPOLE MOMENT DATA; BENZENE SOLVENT, 25°

N_2	d_{12}	ϵ_{12}
5 α -Pregnan-3,20-dione (VI)		
0.000000000	0.873855	2.2748
.000447794	.874108	2.2786
.00103232	.874635	2.2831
.00111081	.874705	2.2837
.00135417	.874764	2.2858
$\alpha = 8.052$	$\beta = 0.744$	$P_e + P_a = 100.08$
$d_1 = 0.87383$	$P_{2\infty} = 203.5$	$\mu = 2.25$
5 α -Pregnane-20-one		
0.000000000	0.873739	2.2743
.00028062	.873838	2.2770
.00047926	.874048	2.2793
.00083567	2.2826
.00115865	0.874348	2.2859
$\alpha = 10.01$	$\beta = 0.553$	$P_e + P_a = 100.12$
$d_1 = 0.87373$	$P_{2\infty} = 233.3$	$\mu = 2.55$

Dipole Moments.—The dipole moments of 5 α -pregnan-20-one and 5 α -pregnan-3,20-dione were run in benzene at 25° and the moment of 3-cholestanone was reported earlier.¹⁰ The data are given in Table I. The dipole moment apparatus used has been previously described.¹⁰ The moments were calculated by essentially the method of Halverstadt and Kumler²⁰ utilizing an IBM 650 computer as previously described.²¹ Because of the high molecular weights of these compounds, an attempt was made to account approximately for atomic polarizability by taking $P_e + P_a = 1.10$ MD, where the latter was found from the table of Vogel.²² The experimental error is ± 0.03 D.

(19) H. Wieland, O. Schlichting and R. Jacobi, *Z. physiol. Chem.*, **161**, 80 (1926).

(20) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(21) N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

(22) A. I. Vogel, W. T. Cresswell, G. J. Jeffrey and J. Leicester, *Chemistry & Industry*, 358 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Ultraviolet Spectra of Several Hydro- and Functional Group Derivatives of Bicycloheptadiene Containing 7-Spiro Substituents

BY CHARLES F. WILCOX, JR., AND RHODA R. CRAIG¹

RECEIVED MAY 2, 1961

The ultraviolet spectra of several spirocyclopropane and spirocyclopentane bridge substituted [2.2.1]bicyclic systems containing olefin and dimethyl maleate chromophores are analyzed. It is shown that these chromophores couple weakly in contrast to the strong coupling in the geometrically related [2.2.1]bicycloheptadiene. The bathochromic shifts caused by bridge substituents increase with their size which can be interpreted either as steric control of the planarity of the maleate chromophore or an increase in the polarizability of the substituents. A probable charge transfer band is identified and its abnormally high intensity discussed. No unique band related to the spirocyclopropane group is observed.

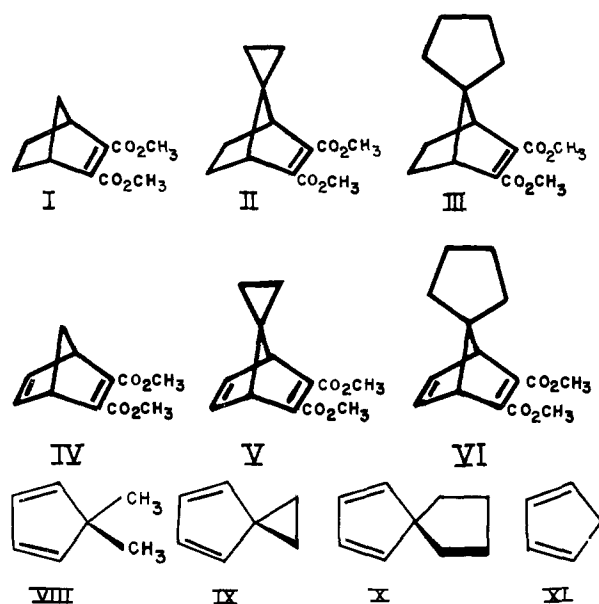
The preparation of various unsaturated [2.2.1]-bicyclic molecules with 7-spirocyclopropane and 7-spirocyclopentane substituents has been described and their ground state properties discussed.² This paper is concerned with the ultraviolet spectra of compounds I, II, III, IV, V, and VI and the degree to which the bridge substituent affects the spectra either by direct interaction with the

maleate or double bond chromophores, or by modifying the interaction between this pair of chromophores. Because of the similar geometry of these molecules to that of bicycloheptadiene VII, whose spectrum has been analyzed,³ these compounds offer further insight into the factors which determine the interaction of non-conjugated chromophores.

(1) Taken from the dissertation submitted by R. R. Craig to Cornell University for the Ph.D. degree, June, 1961.

(2) C. F. Wilcox and R. R. Craig, in press.

(3) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).



Results

The ultraviolet spectra of compounds I through VI in various solvents are recorded in Table I. Also recorded are the ultraviolet spectra of 5,5-dimethylcyclopentadiene (VIII), spiro[2.4]hepta-4,6-diene (IX) and spiro[4.4]nona-1,3-diene (X) in 95% ethanol which will be referred to in the Discussion.

TABLE I

ULTRAVIOLET SPECTRA OF BICYCLIC AND SPIRO OLEFINS					
Compound	Solvent	λ_{\max}	$\log \epsilon$	λ_{\min}	$\log \epsilon$
I	Isooctane	234	3.74		
	EtOH	238	0.67	211	3.53
II	Isooctane	236	3.70		
	EtOH	240	3.69	216	3.59
III	Isooctane	238	3.79		
	EtOH	242	3.77	216	3.59
IV ^a	Isooctane	235	3.36		
	EtOH	237	3.55	219	3.47
V ^a	Isooctane	239	3.52		
	EtOH	240	3.46	226	3.41
VI ^a	Isooctane	243	3.52		
	EtOH	243	3.46	227	3.39
VIII	EtOH	250	3.46	221	1.94
IX	EtOH	257	3.43	^b	
X	EtOH	254	3.44		

^a These compounds show a weak inflection in isooctane and ethanol near 280 $m\mu$. ^b This diene also has a strong maximum at 223 $m\mu$ (3.80) which appears to arise from the interaction of the 200 $m\mu$ Rydberg⁴ diene transition with the 190–210 $m\mu$ cyclopropane transition.⁵

Discussion

From its common occurrence in all six of the bicyclic molecules, I–VI, the band near 240 $m\mu$ can be associated with the α,β -dialkyl substituted maleate chromophore.⁶ It can be deduced from

(4) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); E. P. Carr, *Chem. Revs.*, **41**, 293 (1947).

(5) P. Wagner and A. B. F. Duncan, *J. Chem. Phys.*, **21**, 516 (1953).

(6) Dimethyl α,β -dimethylmaleate, which has a much different steric environment, absorbs at 213 $m\mu$ ($\log \epsilon$ 3.95); R. F. Rekker, P. J. Brombacker, H. Hamann and W. Th. Nanta, *Rec. trav. chim.*, **73**, 410 (1954).

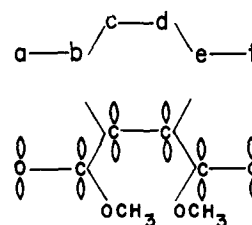


Fig. 1.—Molecular orbital model for the dimethyl maleate chromophore.

the solvent dependence that this absorption involves a shift of charge toward the solvated carboxyl groups. Such a description is supported by both a simple molecular orbital model⁷ and an interacting chromophore model.⁸ In terms of molecular orbitals the wave-functions and corresponding energies for the six π -electron system shown in Fig. 1 are those given in Table II.

TABLE II

ENERGIES AND WAVE-FUNCTIONS OF THE SIX π -ELECTRON SYSTEM OF FIG. 1^a

Orbital	Energy (β)	Wave-function
ψ_6	-1.732	$0.149(\phi_a - \phi_f) - 0.408(\phi_b - \phi_e) + 0.558(\phi_c - \phi_d)$
ψ_5	-1.000	$.289(\phi_a - 2\phi_b + \phi_c + \phi_d - 2\phi_e + \phi_f)$
ψ_4	0.000	$.408(\phi_a - \phi_b - \phi_c + \phi_d + \phi_e - \phi_f)$
ψ_3	+1.000	$.500(\phi_a - \phi_c - \phi_d + \phi_f)$
ψ_2	+1.732	$.558(\phi_a - \phi_f) + 0.408(\phi_b - \phi_e) + 0.149(\phi_c - \phi_d)$
ψ_1	+2.000	$.408(\phi_a + \phi_b + \phi_c + \phi_d + \phi_e + \phi_f)$

^a The coulomb integrals for the oxygen atoms have been set as $\alpha_o = \alpha_c + \beta$.

These wave-functions show that excitation of an electron from the uppermost filled orbital, ψ_3 , to the lowest empty orbital, ψ_4 , moves charge from the center of the chromophore to π -atoms b and e. Since these are the carboxyl carbons and are substituted with methoxy groups it is understandable that solvation of these methoxy groups could cause a bathochromic shift. This same crude description also moves charge from the carbonyl oxygens which might account for why the solvent shift is not as large as it is for the K band of α,β -unsaturated ketones (+11 $m\mu$ vs. about 2³–3 $m\mu$ here).⁹ With the interacting chromophore model essentially this same behavior is predicted since the excitation involves considerable amounts of charge transfer from the ground state of the c,d-double bond to the excited state of the carbonyl chromophore which places the charge largely on the carbonyl carbon.

Perhaps the most striking feature of the bicyclic spectra is that for a given solvent the 240 $m\mu$ band occurs at a nearly constant position largely independent of the bridge substituent or the presence of 5,6-unsaturation. Although excitation energies of about 5 e.v. are involved, the largest variation in λ_{\max} is 9 $m\mu$ which corresponds to a maximum energy difference of only 0.2 e.v. (4 kcal.). Particularly striking is that the average shift which ac-

(7) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952.

(8) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc. (London)*, **A68**, 601 (1955).

(9) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).

companies introduction of a 5,6-double bond into I, II or III to produce IV, V, VI is only 1.5 $m\mu$. It should be recalled that bicycloheptadiene VII with its geometrically similar chromophore system shows a bathochromic shift of about 15–20 $m\mu$ relative to bicycloheptene.⁹ The easiest way to understand these different behaviors is in terms of a simplified interacting chromophore model. For two non-conjugated chromophores which separately absorb energies of E_1 and $E_2 = E_1 - \delta$, respectively, the interacting system will absorb at approximately

$$E = E_1 - \frac{\delta}{2} \pm \sqrt{\Gamma^2 + \left(\frac{\delta}{2}\right)^2}$$

where Γ is the interaction energy of the two transition moment dipoles. In bicycloheptadiene δ is zero so that a shift corresponding to a Γ of about 0.45 e.v. is observed whereas in the present systems the presence of the term $\delta/2$ with a value of about 0.58 e.v. "buffers" the interaction. More than this, because of the smaller coefficients at ϕ_c and ϕ_d in the wave functions ψ_3 and ψ_4 compared with the corresponding coefficients for an isolated double bond, the appropriate value of Γ is reduced by a factor of about $(\sqrt{2})(\sqrt{2})/2\sqrt{6} = 1/\sqrt{6}$. This leads to a predicted shift of the 240 $m\mu$ band of 1.4 $m\mu$, very close to that observed. This treatment assumes that the maleate chromophore is planar. If it were not, as is likely the case, the wavefunctions would differ as would the interaction energy. In the extreme case where the carbomethoxy groups are at right angles to the double bond, Γ has the same value as in bicycloheptadiene and the calculated shift is 7.4 $m\mu$. Because of the smallness of this extreme value the assignment of intermediate twist angles of the carbomethoxy groups from the observed shift is not a reliable procedure. An indirect but sensitive measure is the decrease in $\log \epsilon$ of the 240 $m\mu$ band on incorporation of a 5,6-double bond. For the 240 $m\mu$ band the instantaneous transition dipole of the 5,6-double bond is opposed to the transition dipole of the maleate chromophore so that the greater the mixing, the lower the observed intensity becomes. From the observed average decrease in $\log \epsilon$ of 0.25 on introduction of the 5,6-double bond, an average $\log \epsilon$ of 3.73 for the saturated bicyclics and an assumed $\log \epsilon$ of 4.0 for an isolated double bond, it can be estimated that Γ , which is a measure of the mixing, has a value of 0.29 e.v. This corresponds to carbomethoxy twist angles of 40–45° which is reasonable and a calculated shift in λ_{\max} of 2.3 $m\mu$ which is consistent with the spectral data.¹⁰

A finer examination of the data in Table I reveals small but consistent bathochromic displacements of the 240 $m\mu$ bands as the bridge methylene is successively replaced by a cyclopropane and cyclopentane residue. While these shifts are small and might easily be dismissed as only reflecting our ignorance of the detailed vibrational-rotational structure of the electronic transition, it is tempting to speculate on two other possible explanations. First, if it is assumed that the

(10) This coupled chromophore model can be used to interpret many of the apparently anomalous spectra described by E. R. H. Jones and co-workers, *J. Chem. Soc.*, 4073 (1956).

ground state energies are nearly the same then one reasonable interpretation is that the increasing bulk of the bridge substituents causes increasing restriction of the carbomethoxy groups to conformations more planar with the 2,3-double bond.¹¹ By theory and by observations¹² on related systems it is predictable that the more coplanar maleate chromophore should absorb at longer wave lengths. Unfortunately, a consequence of this coplanarity, a slight increase in extinction coefficient of the 5,6, saturated systems¹³ cannot be checked because of the variable interference of the long wave length tail of higher energy transitions.

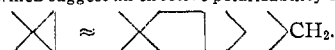
Second, an entirely different explanation can be advanced if it is assumed that the cyclopropane derivatives have sufficiently higher energy ground states such that the excitation energy is really the same or lower than the cyclopentane derivatives. Under these circumstances, where the real order is $\text{Cyclopropane} > \text{Cyclopentane} > \text{CH}_2$, a possible interpretation is that the varying polarizability of the bridge substituent is the determining factor.¹⁴ From the ionization potentials and absorption maxima of cyclopropane, cyclopentane and methane it can be estimated that the polarizability of the groups increases in the stated order.¹⁵ As further support for this interpretation it is significant that VIII, IX and X absorb near 255 $m\mu$ whereas cyclopentadiene XI absorbs at 240 $m\mu$.^{4,16} This 15 $m\mu$ shift which occurs on replacement of two hydrogens in close proximity to the chromophore by alkyl groups can be rationalized similarly in terms of the relative polarizabilities of the substituents.¹⁷ Shifts of comparable magnitude with alkyl substitution of nitrobenzene have been observed previously and given a similar polarizability interpretation.¹⁸

(11) Such an interaction might occur by way of an intervening solvation molecule.

(12) G. W. Gray, Editor, "Steric Effects in Conjugated Systems," Academic Press, Inc., New York, N. Y., especially Chapter 7 and references therein.

(13) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955).

(14) This order is not really essential to this argument if one considers the anisotropy of polarizability. The long-wave length absorption of cyclopropane probably has its transition moment in the wrong direction for polarization by the oscillating dipole of the maleate chromophore so that the effective polarizability could well be intermediate between cyclopentane and methane. See also the comments in footnote 17 which suggest an effective polarizability order of



(15) K. Watanabe, T. Nakayama and J. Mottel, "Final Report on Ionization of Molecules by a Photoionization Method," University of Hawaii, December, 1959; A. Weissberger, Editor, "Techniques of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," Edited by W. West, Interscience Publishers, Inc., New York, N. Y., 1956, p. 646.

(16) It is important here to note that the ca. 240 $m\mu$ transition moment in these *cis*-dienes is perpendicular to the plane of the 5-spiro-substituents just as the predicted moment in the bicyclic systems is perpendicular to the 7-spiro-substituents.

(17) To understand how a polarizability effect could operate in a condensed medium such as the 95% ethanol of this study, it is necessary to realize that the stabilization energy of an oscillating dipole interacting with a polarizable material falls off approximately as $1/r^3$. Thus a 15 $m\mu$ shift arising from a pair of carbon atoms bonded to the ring would become trivially small if these same atoms were removed to a solvent molecule which would necessarily be about twice as distant from the oscillating dipole (because of the van der Waals radii of the poorly polarizable intervening hydrogen atoms).

(18) W. M. Schubert, J. Craven and H. Steadly, *J. Am. Chem. Soc.*, 81, 2695 (1959); A. Buraway and A. R. Thompson, *J. Chem. Soc.*, 4315 (1956).

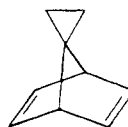
While the choice between the steric or polarizability explanation is not obvious (if indeed either is applicable) it is felt that because of the substituted cyclopentadiene results the steric argument is weak. Further studies of these and other cyclopentadienes directed toward determining the validity of the polarizability argument are in progress.

Another feature of the bicyclic spectra is the occurrence in each of the 5,6-unsaturated compounds IV, V and VI of a weak inflection on the leading edge of the 245 $m\mu$ band. The ϵ_{\max} of these bands was crudely estimated to be in the range of 200–1000 by subtracting from the observed absorption a smooth extrapolation of the 245 $m\mu$ curve. A reasonable interpretation for this extra absorption is that it originates in a transfer of an electron from the ground state of the 5,6-double bond to the lowest energy excited state of the maleate chromophore.¹⁹ The intensity of this band is of some interest. From symmetry considerations of the orbitals involved it is apparent that the transition dipole lies in the direction of a line joining the 1,4-bridgehead carbons even though the electron transfer is at right angles to this direction. The transition moment for this charge transfer can be estimated from the wave functions (planar system) described previously to be approximately $2ReS_{26}/\sqrt{12}$ where R is the length of C=C bond, e is the unit of electrical charge and S_{26} is the overlap integral between the π -orbitals on ring atoms 2 and 6. With an empirical relationship for ϵ_{\max} ,²⁰ appropriate numerical values for the constants, and the calculated value of 0.0834 for S_{26} ,³ the calculated ϵ_{\max} is *ca.* 25. This is not the only source of intensity for this band, however, because the transition moment lies in the same direction as the transition moments of the local excitations of the olefin and maleate chromophores and the transfer band can couple weakly with these excitations by way of the small resonance integral between atoms 2 and 6. The coupling is small but is compensated by the high intensity of these local excitations. Application of first-order perturbation theory leads to a predicted total ϵ_{\max} of $25 + 180 + 235 = 440$ using the same values of β previously used in calculating the spectra of bicycloheptadiene.³

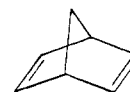
A final point to be made about the bicyclic spectra is that II and V which contain 7-spiro-cyclopropane substituents do not show any extraordinary absorption above 200 $m\mu$ not shown by the corresponding 7-spiro-cyclopentane substituted compounds III and VI. This lack of specific interaction of the cyclopropyl group in the bicyclics compared to the apparently strong interaction in the spiro-diene IX can be understood if the tentative assignment of Wagner and Duncan³ of an in-plane cyclopropane electronic transition moment is accepted. With such a moment the cyclopropane transition is incapable of coupling with the

three bands discussed above because their transition moments are perpendicular to the plane of the cyclopropane ring. It is suggested that with the spiro-diene IX the in-plane cyclopropane transition has a direction such that it can couple strongly with the diene $2p \rightarrow 3s$ out-of-plane Rydberg transition of appropriate symmetry.

It is interesting to note that the ultraviolet spectrum of bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1'-cyclopropane (XII) is in complete accord with the foregoing analysis. This compound was prepared according to the Schmerling procedure²¹ by magnesium iodide dechlorination of the adduct between *cis*-dichloroethylene and the diene IX in 73% yield. This procedure is to be compared with the 55% yield recently reported by Alder, *et al.*,²² for the zinc debromination of the corresponding dibromo adduct. Both the gas phase and the ethanol spectra of diene XII were essentially identical to that reported for the parent diene.³ This lack of interaction of the three-membered ring can



XII



VII

be understood as before in terms of an in-plane cyclopropane transition which has the wrong symmetry to couple strongly to the statically forbidden³ diene transition.

Experimental

The preparation of 2,3-dicarbomethoxybicyclo[2.2.1]hept-2-ene (I), 2,3-dicarbomethoxybicyclo[2.2.1]hept-2-ene-7-spiro-1'-cyclopropane (II), 2,3-dicarbomethoxybicyclo[2.2.1]hept-2-ene-7-spiro-1'-cyclopentane (III), 2,3-dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene (IV), 2,3-dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene-7-spiro-1'-cyclopropane (V), 2,3-dicarbomethoxy-bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1'-cyclopentane (VI), spiro[2.4]hepta-1,3-diene (IX) and spiro[4.4]nona-1,3-diene (X) have been reported² as has the preparation of 5,5-dimethylcyclopentadiene VIII.²³

***cis*-2,3-Dichlorobicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopropane.**—Thirty-one grams (0.33 mole) of *cis*-1,2-dichloroethylene, 20.0 g. (0.22 mole) of 1,3-spiro(2.4)heptadiene and a trace of 2,5-di-*t*-butylhydroquinone were heated together at 170–180° in a sealed ampule for 22–30 hours. After the excess dichloroethylene was removed at reduced pressure, the residual oil was vaporized in a sublimator at 65–75° under a pressure of 4–5 mm. to yield a solid, m.p. (sealed cap.) 96.5–99° after three sublimations, which collected on the cold finger. In each of four runs an average yield of 9.0 g. (22%) was obtained.

Anal. Calcd. for $C_9H_{10}Cl_2$ (189.08): C, 57.17; H, 5.33; Cl, 37.50. Found: C, 57.06; H, 5.31; Cl, 37.29; mol. wt. (camphor), 269.

Bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1'-cyclopropane.—To a stirred mixture of 8 g. (0.33 mole) of magnesium turnings and 160 ml. of anhydrous ether under a nitrogen atmosphere was added during a 0.5-hour period 6.0 g. (0.024 mole) of iodine in three 2-g. portions. A solution of 36.6 g. (0.136 mole) of the *cis*-dichloro adduct in 120 ml. of anhydrous ether was added dropwise over an 11-hour period. The next day the yellow solution was decanted from flocculent precipitate which had formed during the addition of the dichloride. The solid was decomposed with ice-water and then extracted

(19) The long-wave-length bands observed by E. R. H. Jones and co-workers¹⁰ would appear to have an analogous origin. The lower symmetry of their molecules would be expected to lead to higher ϵ_{\max} 's.

(20) W. Kauzmann, "Quantum Chemistry," Academic Press, Inc., New York, N. Y., 1957, p. 582.

(21) L. Schmerling, J. P. Luvisse and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956). We wish to thank Dr. Schmerling for providing further experimental details on their method.

(22) K. Alder, H. Ache and F. H. Flock, *Ber.*, **93**, 1888 (1960).

(23) C. F. Wilcox and M. Mesirov, *J. Org. Chem.*, **25**, 1841 (1960).

with two 150-ml. portions of ether. The original yellow solution and the ether extracts were dried over sodium carbonate and then distilled through a 75-cm. Podbielniak column to yield 11.75 g. of the diene, b.p. 68° (83 mm.), n_D^{20} 1.4871, d_4^{20} 0.9312; lit.²² b.p. 37° (20 mm.).

In ethanol the diene showed absorption, λ_{max} in $m\mu$ (log ϵ) at 207 (3.34), 217 (3.02) shoulder, 223 (2.78) shoulder, 230-243 (2.19) broad step-out. In the vapor the diene

showed some 22 sharp bands between 223 and 200 $m\mu$. The most intense of these lay at 213 $m\mu$.

Anal. Calcd. for C_9H_{10} : C, 91.47; H, 8.53. Found: C, 91.54; H, 8.45.

The ultraviolet spectra were determined on a Cary recording spectrophotometer, model 14, using spectral grade solvents.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

The Wolff-Kishner Reaction with α -Oximinoketones¹

BY HENRY RAPOPORT AND WILLIAM NILSSON²

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The Wolff-Kishner reaction with a number of α -oximinoketones, both cyclic and acyclic, has been investigated. With the acyclic compounds, the major product is normal reduction to the corresponding oxime. However, with the cyclic compounds, both normal reduction to the oxime and *v*-triazole formation may occur, the proportion depending on steric factors. A mechanism for triazole formation has been proposed, based on the observation that substituted hydrazones do not give this reaction.

In a previous communication³ the Wolff-Kishner reaction with α -oximinoketones was reported to yield various types of products depending on the starting material used. Thus, from 2,3-octanedione-3-oxime, a 90% yield of the normal Wolff-Kishner reduction product, 3-octanone oxime, was obtained, while biacetyl monoxime was reported to yield 2,3-butanedione hydrazone oxime. A 70% yield of phenylacetic acid was obtained from α -oximinoacetophenone, and, most interestingly of all, indano[1,2-d]-*v*-triazole was obtained from 1,2-indandione-2-oxime.

A more complete study of this reaction was of interest. In particular, it was desirable to be able to predict the probable product of the Wolff-Kishner reaction with a given α -oximinoketone from structural considerations. Contained within this general question is the more specific one of which α -oximinoketones can be expected to yield triazoles. Furthermore, it was of interest to determine the mechanism of triazole formation under Wolff-Kishner conditions, since this is a new and perhaps convenient method of triazole synthesis.

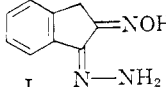
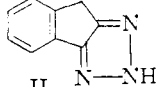
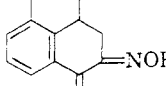
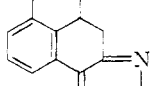
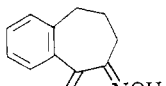
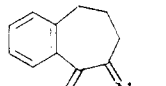
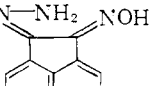
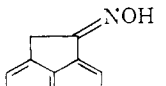
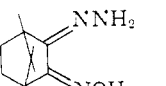
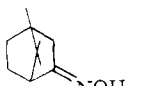
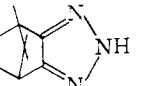
For this purpose we have, in the present work, employed a series of representative cyclic and acyclic, aliphatic and aromatic α -oximinoketones. The reaction conditions employed were, in general, those of the modified Wolff-Kishner reaction⁴ except that the intermediate hydrazones of the α -oximinoketones were isolated and characterized. The hydrazone oxime then was heated at 170-190° for three hours in diethylene glycol containing potassium hydroxide, and the products were separated into neutral, acidic and alkaline fractions.

Results

The results obtained with five cyclic oximinoketones are presented in Table I. In four of the five cases, triazole formation resulted. However,

the yield of triazole significantly decreases as the size of the ketone ring increases from five- to six- to seven-membered, that is as the rings become more flexible and the hydrazone and oxime groups less co-planar.

TABLE I
WOLFF-KISHNER REACTION WITH CYCLIC
 α -OXIMINO-KETONES

Reactant	Products	Yield, %
		52
		34
		15
		32
		58%
		32%

The electronic effect of the fused aromatic ring does not appear to play a role in triazole formation since a significant yield of triazole is obtained

(1) Sponsored, in part, by the United States Atomic Energy Commission.

(2) National Science Foundation Predoctoral Fellow, 1958-1960.

(3) H. Rapoport and H. H. Chen, *J. Org. Chem.*, **25**, 313 (1960).

(4) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).