copy in the n → π* region of the carbonyl chromophore may not also be used for the same type of fingerprinting among steroids. The answer is that low-temperature C.D. measurements are clearly preferable on two grounds.

First, at least two to three times as much material is required in ultraviolet spectrometry of such compounds because of the very low extinction, a drawback which may be quite serious with rare substances. Second, the resolution is not as satisfactory in the −188° absorption spectrum as compared to the C.D. curve measured at such low temperature. As examples, there are included both the room temperature and −188° absorption spectra of cholestan-3-one (III) and of 5α-androstan-3β-ol-17-one (XIX) in Fig. 3 and 13.

The appearance of and the variation in fine structure with changes in temperature and solvent have been attributed, *inter alia*, to the availability of low frequency vibrations and the nature of the solute–solvent interactions. Bayliss and McRae,[23] in particular, have discussed the fine structure of the long wave length n → π* carbonyl transition in terms of the solvent reorientation accompanying the redistribution of charge associated with the electronic promotion in the solute molecule. In terms of their model, the increased fine structure observed for many of the C.D. curves shown here might be attributed in part to a marked slowing down of solvent reorientation times at the lower temperatures in the now more viscous solvents. However, this can be at best only part of the explanation, since other mechanisms, such as the freezing out of low frequency vibrations, are undoubtedly also operative.

(23) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002, 1006 (1954).

Experimental

All measurements were performed in a mixture of ether–isopentane–ethanol in a ratio of 5:5:2 by volume using a Baird-Atomic/Jouan dichrograph operating with a photomultiplier voltage of 1.2 kv. and following the procedures and molecular ellipticity calculations outlined earlier.[4,5,11] A Cary Model 14 spectrophotometer was used for the ultraviolet measurements, using the normal programmed slit width.

Acknowledgment.—Several of the samples originated from the following investigators in connection with earlier O.R.D. measurements in this laboratory: R. C. Cookson (University of Southampton), W. G. Dauben (University of California), E. R. H. Jones (Oxford University), A. Nickon (John Hopkins University), and C. W. Shoppee (University of Sydney). We are greatly indebted to Professor A. Moscowitz (University of Minnesota) for helpful discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY, AMES, IOWA]

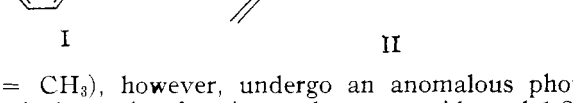
Photoisomerization of 1-Aza-3,5,7-trimethylcyclohepta-4,6-dien-2-one[1]

BY O. L. CHAPMAN AND E. D. HOGANSON

RECEIVED JULY 29, 1963

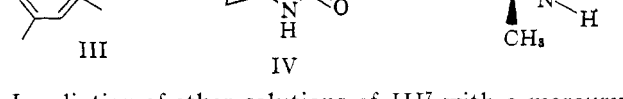
Irradiation of 1-aza-3,5,7-trimethylcyclohepta-4,6-dien-2-one (III) and its N-methyl derivative VII gives in each case a single photoisomer (two stereoisomers are possible) in 70% yield. The photoisomers are shown to be bicyclic valence tautomers by chemical transformations and spectroscopic absorption characteristics. The stereochemistry of the photoisomers is assigned on the basis of the spin coupling constant, J_{45}, and chemical equilibration. The photoisomerization provides a facile synthetic entry to a novel heterocyclic system. Unexpected spin–spin coupling between the C-6 methyl protons and the C-5 proton in IV is detected by double resonance. The N-methyl group of VIII appears as a doublet due to long range coupling to either the proton at C-4 or the proton at C-5.

A variety of conjugated cyclic and acyclic dienes photoisomerize smoothly to cyclobutene derivatives.[2,3] This photoisomerization is particularly useful for conjugated cycloheptadienes.[4,5] 3,5-Cycloheptadienone (I, R = H) and 2-methyl-3,5-cycloheptadienone (I,



I II

R = CH_3), however, undergo an anomalous photochemical reaction forming carbon monoxide and 1,3,5-hexatriene (II, R = H) and 1,3,5-heptatriene (II, R = CH_3).[5,6] The formal similarity between the dienelactam III and the 3,5-cycloheptadienones in placement of trigonal atoms within the seven-membered ring together with the possibility of facile formation of a novel heterocyclic system prompted a study of the photochemistry of III.



III IV

Irradiation of ether solutions of III[7] with a mercury arc lamp encased in a quartz immersion well for 1 hr. gives after removal of the ether and sublimation of the product a single bicyclic photoisomer, m.p. 67–69°, in 70% yield. The photoisomer (osmometric molecular weight 142) shows infrared maxima at 3.15 and 3.27 (N–H), 3.38 and 3.43 (C–H), 5.94 (amide carbonyl), and 6.14 μ (C=C) but no ultraviolet maxima above 220 mμ. Catalytic reduction of the photoisomer gives a saturated dihydro derivative, m.p. 94–95°, 5.90 μ. The photoisomer thus must be bicyclic. Pyrolysis (430°) of the photoproduct gives the starting dienelactam III in 50% yield. This shows the photoprod-

(1) Part X of the photochemical transformations series. For part IX see O. L. Chapman, H. G. Smith, and P. A. Barks, *J. Am. Chem. Soc.*, **85**, 3171 (1963). Portions of this manuscript were taken from the M.S. thesis of E. Hoganson, Iowa State University of Science and Technology, 1963. Similar results have been obtained by L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 500 (1964).

(2) O. L. Chapman, in "Advances in Photochemistry," Vol. I, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(3) P. de Mayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961).

(4) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(5) O. L. Chapman and D. J. Pasto, *Chem. Ind.* (London), 54 (1961); O. L. Chapman, D. J. Pasto, A. A. Griswold, and G. W. Borden, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

(6) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961).

(7) L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962).

TABLE I

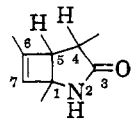
NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Compound	Position 1	2	3	4	5	6	7
III	N–H 0.1	...	H– 7.64 CH_3– 8.70	5.20	CH_3– 8.00	4.57	CH_3– 8.21
VII	N–CH_3 6.97	...	H– 7.66 CH_3– 8.70	5.03	CH_3– 7.93	4.40	CH_3– 8.26
IV	CH_3– 8.61	N–H 1.22	...	H– 7.42 CH_3– 8.87	7.15	CH_3– 8.24	3.85
VIII	CH_3– 8.65	N–CH_3 7.36	...	H– ~7.4 CH_3– 8.94	7.1	CH_3– 8.26	3.84
IX	CH_3– 8.61	N–CH_3 7.34	...	H– 7.84 CH_3– 8.85	7.55	CH_3– 8.29	3.92

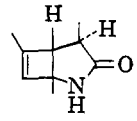
[a] All spectra were taken in carbon tetrachloride containing 1% tetramethylsilane as internal standard. Resonance positions are given in τ-values.

uct to be a valence tautomer (IV) of the diene-lactam III. The structure IV is in accord with the nuclear magnetic resonance spectrum of the photoisomer (Table I). The nuclear magnetic resonance spectrum of IV, moreover, defines the stereochemistry of the photoproduct.

If the C-4 methyl group is *trans* to the C-5 hydrogen (V), the C-4 and C-5 hydrogens will not only be *cis* but



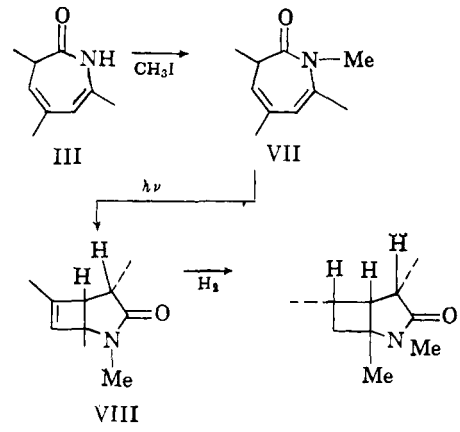
V



VI

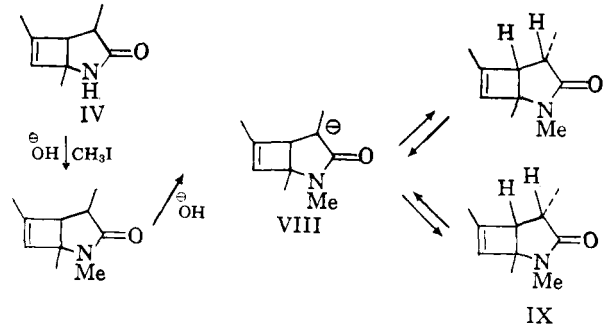
also will be rigidly eclipsed (dihedral angle ~0°). If the C-4 methyl group is *cis* to the C-5 hydrogen (VI), the dihedral angle between the hydrogens at C-4 and C-5 will be approximately 115°. Using the Karplus relationship between dihedral angle and coupling constant one can estimate J_{45} for V at 8–9 c.p.s. and for VI at 1–3 c.p.s.[8,9] The observed value for J_{45} is 9.8 ± 0.5 c.p.s.[10] in agreement with structure V. The nuclear magnetic resonance spectrum of IV shows one unexpected feature. The allylic methyl group (C-6) appears as quartet on slow scan. Double resonance studies show that it is coupled not only to the proton at position 7 but also to the proton at C-5. Saturation of either proton collapses the C-6 methyl quartet to a doublet. It is assumed that the ring fusion is *cis*.[11] The stereochemistry at C-6 in the dihydro derivative is assigned on the basis of steric approach control of the reaction.

Methylation of III with methyl iodide and potassium hydroxide in acetone gives VII. Irradiation of VII gives a single (vapor phase chromatographic analysis) photoisomer (70% yield). Hydrogenation of the photoproduct requires one equivalent of hydrogen. The infrared spectrum and nuclear magnetic resonance spectrum (Table I) of the photoisomer are in accord with structure VIII. The value of J_{45} (9.8 ± 0.5 c.p.s.) is again consistent only with the stereochemistry shown in VIII.[10] The N-methyl group of VIII appears as a doublet (J = 0.67 ± 0.1 c.p.s.) on slow scan. The coupling arises from either the proton at C-4 or the proton at C-5. It was not possible to establish which proton was responsible for the splitting by double resonance because of the proximity of the N-methyl,



VIII

C-4, and C-5 proton resonances. Confirmation of the stereochemistry of VIII and direct interrelation of IV and VIII have been accomplished by methylation of IV under conditions such that the methylation product is equilibrated at C-4. Methylation of IV gives two bicyclic N-methyl lactams in a 10:1 ratio (vapor phase chromatographic analysis). The major product is identical with VIII. The minor isomer IX was not ob-



IX

tained in sufficient quantity for elemental analysis, but the infrared and nuclear magnetic resonance absorption (Table I) of this isomer are very similar to those of VIII. In accord with expectation, $J_{45} < 3$ c.p.s. for the isomer IX. Examination of Dreiding models of VIII and its C-4 isomer shows clearly that VIII with the C-4 methyl group in a quasi-equatorial position is clearly preferred on steric grounds over the isomer in which the C-4 methyl group is rigidly eclipsed with the C-5 hydrogen. The minor isomer IX shows only a broadened singlet for the proton at position 5 as anticipated.

The photochemical behavior of the diene-lactams III and VII clearly parallels the photoisomerization of nor-

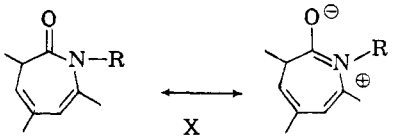
(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(9) H. Conroy, "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 311.

(10) The protons at C-4 and C-5 and the C-2 methyl protons give rise to an ABX_3 pattern. It can be shown readily that J_{AB} can be obtained by first-order methods from the AB region of ABX_n systems although J_{AX} and J_{BX} cannot. The authors are indebted to Dr. R. W. King for discussion of these spectra. Coupling constants were taken from calibrated slow scans of the significant region.

(11) This assumption seems reasonable for the fusion of a four-membered ring to a five-membered ring, although *trans*-fused four- and six-membered rings have recently been prepared: E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963); P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963); J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 597 (1963).

mal conjugated cycloheptadienes[4,5] rather than the anomalous behavior of the 3,5-cycloheptadienones.[5,6] The ultraviolet absorption maximum (252 mμ) of the diene-lactams III and VII is normal and suggests that the diene chromophore can achieve a planar or nearly planar configuration. The correlation of the normal photoisomerization of III and VII with a planar diene chromophore supports the suggestion[6] that the anomalous behavior of 3,5-cycloheptadienones is due to a badly distorted (from planarity) diene chromophore, but it raises the question why the diene chromophore is planar in the diene-lactams III and VII when it is distorted in the 3,5-cycloheptadienones which have a similar disposition of trigonal atoms in the seven-membered ring. The planarity of the diene chromophore in the diene-lactams is probably enforced by the amide group. The steric strain in the planar form is presumably less than the resonance energy of the amide group (X). In a nonplanar structure the resonance



X

stabilization of the amide group would be lost. The carbonyl stretching frequencies (5.98 and 6.00 μ) of the diene-lactams III and VII are normal showing that interaction of the nitrogen unshared pair with the carbonyl group is not impaired.

The stereoselectivity of the photoisomerization of the diene-lactams III and VII is striking and suggests that steric factors can exert a substantial effect on the course of excited state reactions.

Experimental

2-Aza-1β,4α,6-trimethylbicyclo[3.2.0]hept-6-en-3-one (IV).—A solution of III[7] (3.0 g.) in anhydrous ether (1800 ml.) was flushed with nitrogen and then irradiated with a type A Hanovia mercury arc lamp encased in a water-cooled quartz immersion well. After 1 hr. the 252-mμ maximum characteristic of III had completely disappeared, and the irradiation was stopped. Evaporation of the ether gave a thick, brown residue. The residue was distilled (72–74° at 0.7 mm.) giving crystalline IV. Sublimation (50–80° at 0.005 mm.) of the distillate gave pure IV, m.p. 67–69° (2.1 g., 70%). The product showed no ultraviolet maxima in the 220–360-mμ region.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26; mol. wt., 151. Found: C, 71.26; H, 8.72; N, 9.20; mol. wt. (osmometric), 142.

Hydrogenation of IV.—A solution of IV (1.0 g.) in absolute methanol (30 ml.) absorbed 1 equiv. of hydrogen over 10% palladium-on-carbon catalyst at 25°. Filtration and evaporation of the methanol gave the crude dihydro derivative. Sublimation gave pure 2-aza-1β,4α,6α-trimethylbicyclo[3.2.0]heptane, m.p. 94–95° (0.79 g., 78%).

Anal. Calcd. for $C_9H_{15}NO$: C, 70.54; H, 9.87; N, 9.14. Found: C, 70.29; H, 9.88; N, 8.99.

Pyrolysis of IV.—A solution of IV (0.3 g.) in *n*-hexane (25 ml.) was dropped slowly into a vertical, 6 in. by 0.75 in., Pyrex helices packed pyrolysis column preheated to 430°. The column was swept with oxygen-free nitrogen, and the pyrolysate was collected in a trap immersed in Dry Ice–acetone. After cooling, the column was washed with acetone, and the acetone solution was combined with the pyrolysate. Evaporation of the acetone gave a brown solid. Recrystallization of this solid from aqueous ethanol gave III, m.p. 132–133° (0.15 g., 50%), which was identical in infrared and ultraviolet absorption with authentic III.

Methylation of III.—A solution of III (5.0 g.) and potassium hydroxide (6.50 g.) in acetone (150 ml.) was refluxed gently while methyl iodide (10 g.) was added slowly with stirring. After 15 min. the acetone was evaporated, and water was added to the residue. Extraction with ether, drying, and removal of the ether gave a colorless liquid. Distillation (58° at 0.5 mm.) of the crude product gave pure (vapor phase chromatographic analysis) VII (4.4 g., 80%); λ_{max} 95% EtOH 252 mμ (4540), 6.00 μ (amide carbonyl group).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.47. Found: C, 72.79; H, 8.96; N, 8.50.

2-Aza-1β,2,4α,6-tetramethylbicyclo[3.2.0]hept-6-en-3-one (VIII).—A solution of VII (5.0 g.) in anhydrous ether (1800 ml.) was flushed with nitrogen and irradiated with a type A Hanovia mercury arc lamp encased in a water-cooled quartz immersion well. After 1 hr. the 252-mμ absorption characteristic of VII had disappeared, and the irradiation was stopped. Evaporation of the ether and distillation of the product gave VIII (3.5 g., 70%, homogeneous to vapor phase chromatography). This product was identical in infrared and nuclear magnetic resonance absorption and vapor phase chromatographic retention with the major product of the methylation of IV (see below).

Anal. Calcd. for $C_{10}H_{15}NO$ (VIII): C, 72.69; H, 9.15; N, 8.47. Found: C, 72.88; H, 9.33; N, 8.24.

Methylation of IV.—A solution of IV (1.0 g.) and powdered potassium hydroxide (1.3 g.) in acetone (25 ml.) was refluxed gently while methyl iodide (1.4 g.) in acetone (20 ml.) was added slowly with stirring. After 15 min. the acetone was evaporated, and water was added to the residue. Extraction with ether, drying, removal of the ether, and distillation (49–55° at 0.25 mm.) gave a 10:1 (vapor phase chromatographic analysis) mixture of VIII and IX. Preparative scale vapor phase chromatography (15% diethyl succinate on Chromosorb P at 134°) gave the major product VIII and trace amounts of IX. Both products showed infrared carbonyl absorption at 5.93 μ.

Acknowledgment.—The authors are indebted to the National Science Foundation for partial financial support (NSF-G15832) of this research. Ultraviolet spectra were recorded with an instrument made available by a grant (NSF-G14916) from the National Science Foundation. The authors wish to thank Dr. L. A. Paquette for informing them of his results prior to publication.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN CO., KALAMAZOO, MICH.]

Dihydroazepinone Chemistry. VI. The Photoisomerization of 1,3-Dihydro-3,5,7-trimethyl-2H-azepin-2-one[1]

BY LEO A. PAQUETTE[2]

RECEIVED JULY 29, 1963

The photolysis of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (I) has been found to afford a single isomer of 1,4,6-trimethyl-2-azabicyclo[3.2.0]hept-6-en-3-one (II). The structure of this photoisomer has been elucidated from its n.m.r. spectrum. Several transformations of II are described, including its conversion to 1,2,4,6-tetramethyl-2-azabicyclo[3.2.0]heptane hydrochloride (V), a novel bicyclic amine.

In previous papers of this series,[3,4] the one-step ring expansion of sodio 2,6-disubstituted and 2,4,6-trisubstituted phenoxides to the novel 1,3-dihydro-2H-azepin-2-ones by the use of chloramines was discussed. Closer examination of the structure of this class of compounds show them to be heterocyclic 1,3-cycloheptadienes and, as such, they should be capable of photolytic excitation.

(1) Part V: L. A. Paquette, *Tetrahedron Letters*, **No. 29**, 2027 (1963).

(2) Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

(3) L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962).

(4) L. A. Paquette, *ibid.*, **85**, 3288 (1963).