mixture by integration of its quartet at δ 0.00 ppm (1 H) using the entire aromatic region (4 H) as an internal standard. The relative per cent yields of cycloprop[2,3]indene, 1,2-dihydronaphthalene, 1-methylindene, and 3-methylindene were then determined from glpc data. The actual yields of these materials were calculated by reference to the yield of cycloprop[2,3]indene obtained by nmr examination of the product mixture.

Registry No.—1, 15677-15-3; NBS, 128-08-5; Br_2, 7726-95-6; bromotrichloromethane, 75-62-7; tri-*n*-butyltin hydride, 688-73-3; triphenyltin hydride, 892-20-6.

Acknowledgment.—The authors are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Academic Senate Committee on Research of the University of California, Davis, for partial support of this research.

Azo Compounds. 1. The Synthesis and Decomposition of 3,3'-Diphenyl-5,5'-bi-1-pyrazoline[1,2]

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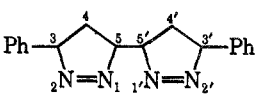
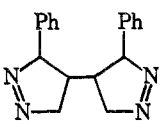
The only product isolated from the reaction of phenyldiazomethane with 1,3-butadiene was a mixture of three stereoisomers of 3,3'-diphenyl-5,5'-bi-1-pyrazoline (I). The thermal and photochemical decompositions of I and of one of the stereoisomers isolated in tlc homogeneous form are described.

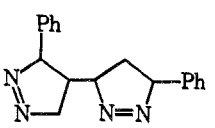
Despite a number of investigations[4-9] on the pyrolysis and photolysis of 1-pyrazolines, it has not been possible to completely generalize the mechanism of these decompositions. We report herein the formation and the decomposition of 3,3'-diphenyl-5,5'-bi-1-pyrazoline (I), obtained as a mixture of three isomers. The isolation of one of these isomers (Ia or Ib) in tlc homogeneous form, as well as its decomposition, is also described.



I



II



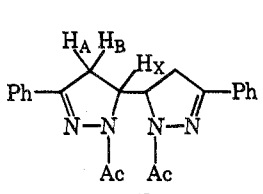
III

Results and Discussion

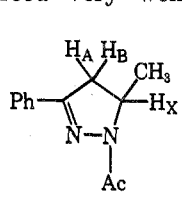
1. Synthesis and Assignment of Structure.—The reaction of diazoalkanes with olefins affords five-membered cyclic azo compounds in fair yields.[5-12] 3-Vinyl-1-pyrazoline has been prepared recently by this method.[11] Our attempts to prepare the 3-phenyl-5-vinyl-1-pyrazoline by the reaction of phenyldiazomethane with 1,3-butadiene resulted only in the formation of a 2:1 adduct, as shown by the elemental analysis. Three types of adducts (I, II, and III) are possible, depending on the direction of addition of phenyldiazomethane. Structure I was assigned to the product isolated on the basis of its spectral data.

The cis-azo linkage was confirmed by its ultraviolet absorption at 328 mμ and by a sharp band at 1540 cm^{-1} in the infrared. These values are in agreement with those previously reported for monocyclic 1-pyrazolines.[4-8,10,13-17] The lack of NH absorption in the infrared spectrum also indicated the absence of isomeric hydrazone.

The presence of several complex splitting patterns in the nmr spectrum of I did not allow unambiguous distinction between structures I, II, and III. To facilitate the nmr analysis, I was converted to the 1,1'-diacetyl-bi-2-pyrazoline derivative (IV) by acid-catalyzed isomerization and acetylation. The coupling constants J_{AB}, J_{AX}, and J_{BX} for IV agreed very well with



IV



V

(1) This is the 50th in a series of papers concerned with the preparation and decomposition of azo compounds. See previous paper in this series by C. G. Overberger and J. Stoddard, *J. Amer. Chem. Soc.*, in press.

(2) This paper comprises a portion of a dissertation submitted by R. Zangaro in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn, 1968.

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(4) C. G. Overberger and J.-P. Anselme, *J. Amer. Chem. Soc.*, **86**, 658, 5364 (1964).

(5) C. G. Overberger, R. E. Zangaro, and J.-P. Anselme, *J. Org. Chem.*, **31**, 2046 (1965).

(6) C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **87**, 4119 (1965).

(7) (a) K. L. Rinehart, Jr., and T. van Auken, *ibid.*, **82**, 5251 (1960); (b) T. van Auken and K. L. Rinehart, Jr., *ibid.*, **84**, 3736 (1962).

(8) (a) R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); (b) R. J. Crawford, A. Mishra, and R. J. Dummel, *ibid.*, **88**, 3959 (1966); (c) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (d) R. J. Crawford and G. L. Erickson, *ibid.*, **89**, 3907 (1967).

(9) H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 483 (1962).

(10) C. G. Overberger and J.-P. Anselme, *ibid.*, **84**, 869 (1962).

(11) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967); see also P. K. Kadaba, *Tetrahedron*, **25**, 3053 (1969).

(12) (a) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966); (c) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

(13) J. A. Moore, *J. Org. Chem.*, **20**, 1607 (1955).

(14) (a) D. E. McGreer, *ibid.*, **25**, 852 (1960); (b) D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *Can. J. Chem.*, **43**, 1398 (1965); (c) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *ibid.*, **43**, 1407 (1965).

(15) G. P. Mueller and B. Riegel, *J. Amer. Chem. Soc.*, **76**, 3686 (1960).

(16) R. Wiechert and E. Kaspar, *Chem. Ber.*, **93**, 1710 (1960).

(17) J. A. Moore, W. F. Holton, and E. L. Wittle, *J. Amer. Chem. Soc.*, **84**, 390 (1962).

those of *N*-acetyl-3-phenyl-5-methyl-2-pyrazoline (V).[18] These data are summarized in Table I. The ABX type

TABLE I
NMR DATA OF 2-PYRAZOLINES IV AND V[a]

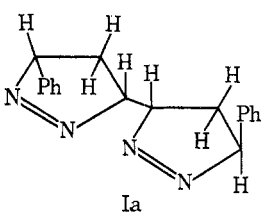
2-Pyrazoline	H_A	H_B	H_X[b]	J_{AX}	J_{BX}	J_{AB}
IV	6.52	7.00	4.80	10.5	5	18
V	6.73	7.35	5.44	10.5	5	17

[a] Peak positions determined at 60 MHz in $CDCl_3$ (at 59°) and are given in τ values (TMS internal standard); J values are in Hz. [b] These values are in fair agreement with those reported by Hassner and Michelson for similar compounds [*J. Org. Chem.*, **27**, 3794 (1962)].

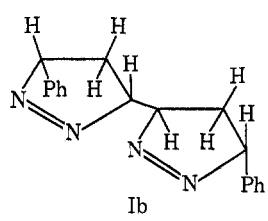
splitting pattern of V was similar to that of the 1,1′-diacetyl-bi-2-pyrazoline derivative (IV).

In contrast, the diacetyl dihydrazone pyrazoline derived from 3,3′-diphenyl-4,4′-bi-1-pyrazoline (II) would exhibit an ABX type pattern having the relative chemical shifts of the H_X and the H_A and H_B protons reversed. If IV had resulted from the other possible adduct (III), a more complex spectrum of two overlapping ABX patterns would have been anticipated.

The bi-1-pyrazoline I has four asymmetric centers (at carbon atoms 3, 3′, 5, and 5′) and, therefore, can exist as four *dl* pairs distributed as cis,cis, trans,trans, and two cis–trans geometric isomers and two meso isomers (cis,cis and trans,trans). Thin layer chromatography of analytically pure I indicated the presence of three components. The separation of the major of these as a homogeneous compound by thin layer chromatography was accomplished by repeated column chromatography over silica gel; elution with dichloromethane afforded an isomer, mp 167–168°. Although tlc homogeneity does not assure the presence of a single isomer, none of the available evidence suggested that this crystalline material was still a mixture of isomers. The structure was tentatively assigned as cis,trans, *i.e.*, as either *meso*-3,3′-diphenyl-*dl*-5,5′-bi-1-pyrazoline (Ia) or *dl*-3,3′-diphenyl-*meso*-5,5′-bi-1-pyrazoline (Ib) based on the nmr spectrum which indicated a nonequivalence of the two pyrazoline rings (in each of the other four diastereomeric choices, *i.e.*, the two isomers of *meso*-3,3′-diphenyl-*meso*-5,5′-bi-1-pyrazoline and the two isomers of *dl*-3,3′-diphenyl-*dl*-5,5′-bi-1-pyrazoline, the two pyrazoline rings are in equivalent environments). In particular, the benzylic protons are cen-



Ia



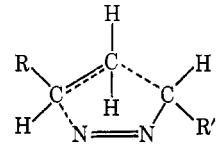
Ib

tered at τ 4.25 and consist of two overlapping "quartets" instead of a simple four-line pattern as would be expected if both rings were equivalent. Similarly, the protons at carbon atoms 5 and 5′ appear as a complex multiplet (centered at τ 4.25) apparently complicated by splitting due to H_5–$H_{5'}$ interaction which would occur only if both rings were nonequivalent.

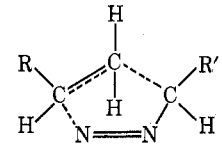
(18) (a) K. von Auwers and P. Heimke, *Justus Liebigs Ann. Chem.*, **458**, 186 (1927); (b) R. C. Fuson, R. E. Christ, and G. M. Whitman, *J. Amer. Chem. Soc.*, **58**, 2450 (1936).

It was not possible to further distinguish between the two possible structures Ia and Ib on the basis of the available data.

It would be difficult to apply the concerted transition states (VIa or VIb) postulated for 1,3-dipolar additions for the formation of Ia or Ib; indeed in either case (Ia or Ib), one of the two cycloaddition steps would require an unfavorable cis addition. A plausible explanation

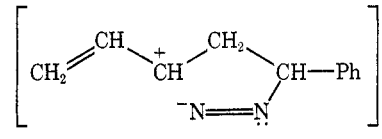


VIa



VIb

which might account for the experimental observations would involve the stepwise formation of the initial five-membered ring[6] *via* a stabilized intermediate such as VII, thus allowing bond rotation to occur prior to



VII

ring closure. This might result in the formation of both *cis*- and *trans*-3-phenyl-5-vinyl-1-pyrazoline (1:1 adduct). The addition of the sceond phenyldiazomethane to the 1:1 adduct could occur in the usual trans manner (involving a transition state such as VIa), thus leading (at least in part) to the formation of the *meso–dl* isomer of bi-1-pyrazoline. The use of lower temperatures and shorter reaction times failed to produce a 1:1 adduct 3-phenyl-5-vinyl-1-pyrazoline. The attempted addition of vinyldiazomethane[19,20] to styrene gave a high yield of pyrazole.

2. Thermal and Photolytic Decomposition.—The mixture of stereoisomers of 3,3′-diphenyl-5,5′-bi-1-pyrazoline (I) and the pure isomer (Ia,b) were each decomposed thermally and photochemically in solution. The decomposition products in each case were shown to be mixtures of isomers of 2,2′-diphenylbicyclopropane (VIII) by their infrared (1025 cm^{-1}) and nmr (τ 9.0–9.5) spectra and by their elemental analyses. No other hydrocarbon products were evident.

VIII

The per cent composition of bicyclopropyls varied slightly with conditions. The results are summarized in Table II. (The bicyclopropanes VIIIa–c are listed in order of increased vpc retention time.)

The results of the thermal and photochemical decompositions of the isomer mixture I indicated that in this case there was very little difference (essentially the same ratio for VIIIa:VIIIb:VIIIc, 5.2:1:6.2) in product selectivity between the two processes. The thermal decomposition of pure isomer Ia,b gave the same three products, but in a ratio of 6.1:1:9.4. On the other hand, photolysis of Ia,b in solution showed

(19) I. Tabushi, K. Takagi, M. Okano, and R. Oda, *Tetrahedron*, **23**, 2621 (1967).

(20) C. D. Hurd and S. C. Lui, *J. Amer. Chem. Soc.*, **57**, 2656 (1935).

TABLE II
DECOMPOSITIONS OF 1-PYRAZOLINES[a]

1-Pyrazoline	Conditions	VIIIa	VIIIb	VIIIc
I (isomer mixture)	Thermal	42.2	7.3	50.5
	Photolytic	41.1	9.0	49.9
Ia,b (pure isomer)	Thermal[b]	36.9	6.1	57.0
	Photolytic[c]	12.0	0.0	88.0

[a] The thermal decompositions were carried out in *p*-xylene at the reflux temperature (145°); the photolyses were run in a Pyrex apparatus in dioxane at ~15°. [b] Very little difference (37.1:5.8:57.1) was observed at 110°. [c] Photolysis of a vigorously stirred suspension in *n*-hexane at ~15° gave essentially similar results (9.6:0.0:90.4).

enhanced product stereoselectivity affording only two of the three bicyclopropanes (VIIIa and VIIIc) in a ratio of 1:7.4. It is interesting to note that a large portion of VIIIa and all of VIIIb are apparently formed photochemically from one or both of the other two isomers present in the mixture. The data available did not allow a stereochemical assignment to these isomers.

Experimental Section

Melting points are reported as uncorrected. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany. Nmr spectra were obtained on a Varian Associates Model A-60 spectrometer using tetramethylsilane as internal standard, at room temperature except where noted otherwise. Infrared spectra were run on a Perkin-Elmer Model 521 spectrophotometer. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. All vapor phase chromatographic analyses were performed on a Varian Aerograph Model 1520 (2 m × 0.25 in. o.d. column packed with 15% DC-710 silicone grease on firebrick) using the thermal conductivity detectors. The instrument was operated isothermally at 150° for 90 min and then programmed at 50°/min to a maximum temperature of 225° and held at this temperature until the samples eluted. All preparative vapor phase chromatography was performed on a Varian Aerograph Model A-700 (20 ft × 3/8 in. o.d. column packed with 20% SE-30 silicone gum rubber on 60–80 mesh Chromosorb W, DMCS).

3,3'-Diphenyl-5,5'-bi-1-pyrazoline (I).—One liter of a freshly prepared 0.35 *M* solution of phenyldiazomethane[21] was poured into a 3-l., three-neck, round-bottom flask, equipped with a magnetic stirring bar, gas inlet tube, and gas outlet connected to a bubble counter containing a small amount of mercury. Anhydrous ether was added to bring the total volume to 1.5 l. 1,3-Butadiene was passed slowly into the stirred solution at such a rate as to cause intermittent bubbling of the mercury in the bubble counter. The flask was then wrapped completely in aluminum foil and the reaction allowed to proceed at room temperature for 24 hr. After this time, a small amount of material began to crystallize. The flow of butadiene was stopped and the flask was cooled in a Dry Ice–trichloroethylene bath for 1 hr. The precipitate (10 g) was filtered and washed with cold pentane to remove the adhering red color. The filtrate (containing unreacted phenyldiazomethane) was returned to the 3-l. flask and the flow of 1,3-butadiene was resumed and continued for an additional 24 hr to give an additional 5 g of product. The total yield of 3,3'-diphenyl-5,5'-bi-1-pyrazoline (I) amounted to 15 g (29% based on phenyldiazomethane) of a mixture of isomers, mp 152–155°. Three recrystallizations from methanol gave a constant melting sample: mp 156–157°; ir 1540 cm^{-1} (N=N); uv λ_{max} 328 mμ (ε 565). This material proved stable for extended periods of time when stored in a desiccator at −20°.

Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.45; H, 6.25; N, 19.30. Found: C, 74.52; H, 6.36; N, 19.31.

Chromatographic Analysis of I and Isomer Separation.—A solution of 1 mg of the freshly recrystallized 3,3'-diphenyl-5,5'-bi-1-pyrazoline mixture (I) in 0.5 ml of dichloromethane was prepared and 3 μl of this solution (equivalent to 6 μg of I) was spotted on a plate. The tlc plates consisted of a 250-μ layer of silica gel (5% $CaSO_4$ binder) on a 50 × 200 mm glass plate. The sample was eluted with a mixture of 3 parts benzene, 3 parts dichloromethane, and 1 part methanol by volume and detected by exposure of the plate to iodine vapor. Three spots were observed; the R_f values were 0.73, 0.69, and 0.66.

A column (20 mm i.d. × 400 mm length) was packed with 50 g of silica gel (particle size 0.05–0.2 mm) in a slurry of dichloromethane. Tight packing was assured by the use of an electric vibrator until the column did not appear to settle further.

A solution of 1 g of 3,3'-diphenyl-5,5'-bi-1-pyrazoline (I), in warm dichloromethane was placed on the column and eluted with 2.0–2.5 l. of dichloromethane. Tlc analysis of the fractions, mp 164–165°, indicated a predominance of the isomer with the highest R_f value and only small amounts of the other two isomers. These fractions were combined and chromatographed as before and gave the pure isomer, mp of 167–168° dec, homogeneous by thin layer chromatography (R_f 0.73). (Rechromatography or recrystallization from methanol did not raise the melting point.) The ir spectrum of this substance contained a band at 1540 cm^{-1} (N=N) and its uv spectrum exhibited an absorption at 328 mμ (ε 563). The nmr spectrum (DMSO-d_6, 70°) exhibited resonance as follows: τ 2.7 (10 H, C_6H_5), 4.25 (2 H, PhCH, 2 overlapping quartets), 4.75 (2 H, NCHCHN, complex multiplet), and 8.2 (4 H, CH_2, complex multiplet).

Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.45; H, 6.25; N, 19.30. Found: C, 74.54; H, 6.31; N, 19.13.

1,1'-Diacetyl-3,3'-diphenyl-5,5'-bi-2-pyrazoline (IV). A. From I (Mixture of Isomers).—A mixture of 3 g (10 mmol) of freshly recrystallized I, 50 ml of acetic anhydride, and several crystals of *p*-toluenesulfonic acid was stirred at room temperature for 48 hr. The mixture was then heated to 80° for 2 hr until all solid material had dissolved. On slow cooling, the solution deposited 0.5 g of a white solid, mp 215–220°. Evaporation of the filtrate gave an additional 0.6 g of a white solid, mp 210–217°. An analytical sample of IV, mp 218–219°, was obtained by recrystallization from methanol: nmr ($CDCl_3$, 59°) τ 2.3 (10 H, C_6H_5), 4.8 (2 H, CH quartet), 6.7 (4 H, CH_2 multiplet), and 7.8 (6 H, CH_3CO, singlet).

Anal. Calcd for $C_{22}H_{22}N_4O_2$: C, 70.57; H, 5.92; N, 14.96. Found: C, 70.55; H, 5.78; N, 15.04.

B. From I (Pure Isomer).—To 100 mg (0.34 mmol) of the pure isomer of VI (mp 167–168°) was added 10 ml of acetic anhydride and a crystal of *p*-toluenesulfonic acid. The mixture was stirred and heated to about 40°, at which temperature the bi-1-pyrazoline completely dissolved. The solution was maintained at 40–50° for 3 hr. The excess acetic anhydride was then removed under vacuum. The product, obtained as a brownish-yellow powder, was taken up in hot 1:1 methanol–water. On cooling, 56 mg of a yellow powder, mp 185–190°, was obtained. A solution of this material in hot methanol, when allowed to crystallize very slowly, gave white crystals, mp 215–218°, identical (ir and mixture melting point) with that sample of IV prepared from I (isomer mixture).

Isolation and Determination of the Decomposition Products of I.—A solution of 10 g of I in *p*-xylene was heated under reflux for approximately 6 hr. After removal of the solvent by distillation, the residue was distilled at 0.2 mm and the products were collected as a liquid, bp 125–140°. Gas chromatographic analysis indicated the presence of three products. The vpc retention times were 149, 157, and 173 min, and separation was effected by preparative vpc. Repurifications by vpc and short-path distillation at 1 × 10^{-5} mm gave products of better than 99% purity. The isomer with the shortest retention time (VIIIa) exhibited a λ_{max} at 221 mμ (ε 23,300) and an infrared band at 1026 cm^{-1}. The nmr spectrum (CCl_4) showed peaks at τ 2.8 (10 H, C_6H_5), 8.0 (2 H, PhCH, multiplet), and 9.1 (6 H, $CHCH_2$, multiplet).

Anal. Calcd for $C_{18}H_{18}$: C, 92.25; H, 7.75. Found: C, 91.97; H, 7.80.

The isomer with intermediate vpc retention time (VIIIb) exhibited a λ_{max} at 220 mμ (ε 20,800) and an infrared band at 1026 cm^{-1}. The nmr spectrum (CCl_4) showed resonance at τ 2.8 (10 H, C_6H_5), 8.0 (2 H, PhCH, multiplet), and 9.1 (6 H, $CHCH_2$, unresolved multiplet). The isomer with the longest retention time (VIIIc) exhibited a uv absorption at 223 mμ (ε 21,200) and an ir band at 1026 cm^{-1}. The nmr (CCl_4) showed peaks at τ 2.9 (10 H, C_6H_5), 8.2 (2 H, PhCH, multiplet), and 9.1 (6 H, $CHCH_2$, multiplet).

Quantitative Determination of the Products from the Thermal Decomposition of I and VI.—The *p*-xylene (Matheson Coleman

(21) J.-P. Anselme, *Org. Prep. Proced.*, **1**, 73 (1969).

and Bell, chromatographic quality) used as a solvent for the decompositions was dried by storage over activated molecular sieves and deoxygenated by bubbling purified nitrogen for 12 hr.

Samples (50–100 mg) of freshly recrystallized I or VI were weighed into a 5-ml glass ampoule kept under nitrogen and 2 ml of *p*-xylene was added. The system was then degassed by the freeze–vacuum–thaw method (3 times). The ampoule was sealed while the contents were frozen and still under high vacuum and then heated by the refluxing vapors of either xylene or toluene depending on the decomposition temperature desired. When decomposition was complete, the tube was allowed to cool and the solvent removed by freeze drying. In all cases, quantitative yields of bicyclopropyls (IX) were obtained. The ratios of products were determined by gas chromatography and results are summarized in Table II.

Quantitative Determination of the Products from the Photolytic Decomposition of I and VI in Solution.—The photolytic decompositions were carried out on approximately 50–100 mg of the freshly recrystallized I isomer mixture or pure isomer Ia,b dissolved in 30–40 ml of spectroquality dioxane. These solutions were irradiated in a Pyrex apparatus[22] (care was taken to exclude oxygen) with a Rayonet ultraviolet reactor (lamps with maximum emission at 350 nm were used). Nitrogen evolution was measured in a thermostated gas buret. Cessation of nitrogen evolution was taken as the end of the decomposition. In all cases, 95–100% of the theoretical nitrogen was evolved. After removal of the dioxane by freeze drying, the products were analyzed as before. Bicyclopropyls VIII were isolated in quantitative yields. The results are summarized in Table II.

Registry No.—*cis,trans*-I, 27694-29-7; IV, 27825-09-8; VIII, 27755-39-1.

Acknowledgment.—The authors gratefully acknowledge financial support of the National Science Foundation, Grant No. GP-7600.

(22) C. D. DeBoer, N. J. Turro, and G. S. Hammond, *Org. Syn.*, **47**, 65 (1967).

Ring Expansion of a 1,2-Dihydropyridine to an Azepine

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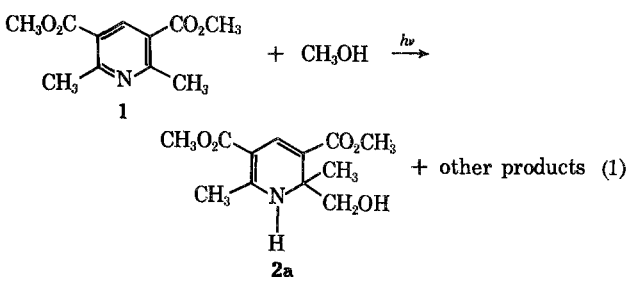
Ring expansion of the tosylate of 3,5-dicarbomethoxy-2,6-dimethyl-2-hydroxymethyl-1,2-dihydropyridine (**2b**) is described. The product is 4,6-dicarbomethoxy-2,7-dimethyl-3*H*-azepine (**3**) which, in polar solvents, is in equilibrium with its dimer **5** formed by addition of the 2-methyl group of **3** to the N_1–C_2 double bond of another molecule of **3**. The structure of **3** is established from the nmr spectrum of its hydrogenation product. Ring expansion proceeds with the exclusive migration of a vinylic group (C_2–C_3 bond) of **2b** with no concomitant migration of the nitrogen atom. In the presence of diethylamine, **3** condenses with benzaldehyde to give 4,6-dicarbomethoxy-7-methyl-2-(*trans*-styryl)-3*H*-azepine (**8**). The nmr spectra for the methylene groups of both **3** and **8** are temperature dependent indicating ring-inversion barriers of $\Delta G^{\ddagger} = 13.7$ kcal/mol and $\Delta G^{\ddagger} = 14.2$ kcal/mol, respectively; no evidence of valence tautomerism was found. Limitations of this ring-expansion procedure are discussed.

Methanol adds to the pyridine derivative **1** upon irradiation yielding 1,2-dihydropyridine **2a** (eq 1).[1] The

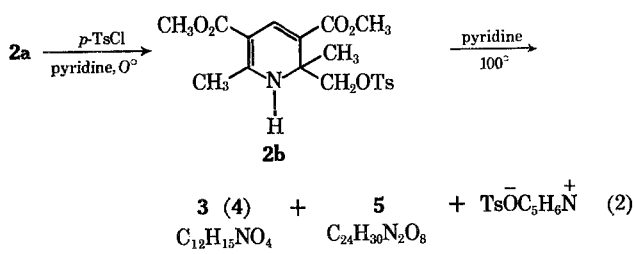


(1)

hydroxy methyl group of **2a** provides an obvious point at which to trigger ring expansion with either a vinylic group (C_2–C_3 bond) or the nitrogen atom (N_1–C_2 bond) being properly situated for a 1,2 shift.[2] We report here the successful ring expansion of the tosylate **2b** and subsequent transformations of the rearrangement product.

Results

Dihydropyridine **2a**, which is stable at room temperature,[3] is obtained readily from other photochemical reaction products (eq 1) by thick layer chromatography (tlc). Tosylation of **2a** in pyridine in the cold gives the tosylate **2b** (eq 2); no substitution is observed at nitrogen consistent with the normal selectivity of tosyl chloride.[4] On heating at 100° in pyridine, **2b** reacts rapidly to produce *p*-toluenesulfonic acid (isolated in 85% yield as the pyridinium salt) and two neutral compounds one of which, isolated by tlc in 40–50% yield, was a rather unstable oil tentatively considered to be either 3*H*-azepine **3** or 2*H*-azepine **4**.[5] The neutral compound **5**, obtained in 18% yield, was a solid, mp 138–140°. The



(2)

(1) R. M. Kellogg, T. J. van Bergen, and H. Wynberg, *Tetrahedron Lett.*, 5211 (1969). The plethora of products which may be obtained from the photochemical reactions of pyridines are described in this article. Full details will be published in due course.

(2) For a review of ring-expansion reactions, see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

(3) (a) Most 1,2-dihydropyridines are notorious for their instability. See, for example, W. Traber and P. Karrer, *Helv. Chim. Acta*, **41**, 2066 (1958). (b) See, for a review on dihydropyridines, R. A. Barnes, "Pyridine and Derivatives," part I, E. Klingsberg, Ed., Interscience, New York, N. Y., 1960.

(4) L. F. Fieser and M. Fieser, "Reagents For Organic Synthesis," Wiley, New York, N. Y., 1968, p 1180.

(5) We felt it inadvisable to distil this compound in order to obtain an analytical sample; identification is based on spectral properties and chemical transformations (*vide infra*). Satisfactory elemental analyses were obtained for all of its precursors and derivatives.