distillates which solidified at room temperature were recrystallized from a mixture of benzene and hexane (3:1). After two recrystallizations, 1.97 g (10.2%) of yellow crystals (mp 72.5–73.8°) was obtained. If the preliminary purification by washing through alumina is omitted, the distilled ester is oily and can be crystallized only with difficulty.

*Anal.* Calcd for $C_6H_7N_3O_2$: C, 47.05; H, 4.61; N, 27.43; mol wt, 153.1. Found: C, 47.16; H, 4.71; N, 27.43; mol wt, 155 (osmometric).

An increase in the addition time of the ethyl oxalamidrazonate to the glyoxal solution to 36 hr eliminated the formation of compound **4** (R = –H) without increasing the yield of the triazine ester.

**1,2,4-Triazine-3-carboxylic Acid** (**6**).—To a stirred solution of 504 mg of ethyl 1,2,4-triazine-3-carboxylate in 8 ml of absolute ethyl alcohol was added a filtered solution of 0.3 g of potassium hydroxide in 15 ml of absolute ethyl alcohol. The resulting solution was allowed to stand at room temperature for 24 hr. The precipitated solid (**5**) (522 mg; 97% of theory) was collected and recrystallized from 95% ethyl alcohol. The small pale yellow crystals melted at 250–280° with decomposition. Additional recrystallizations from the same solvent did not alter the decomposition range.

*Anal.* Calcd for $C_4H_2KN_3O_2$: C, 29.43; H, 1.23; N, 25.75. Found: C, 29.52; H, 1.22; N, 25.50.

The free carboxylic acid was obtained by dissolving the potassium salt **5** (231 mg; 1.42 mmoles) in 1.0 *N* aqueous hydrochloric acid (1.5 ml). The resulting solution was freeze-dried and the residue was collected, washed with a few drops of water, air dried, and finally dried under vacuum over phosphorus pentoxide.

*Anal.* Calcd for $C_4H_5N_3O_3$: C, 33.57; H, 3.52; N, 29.37. Found: C, 32.91; H, 3.09; N, 29.15 (see text).

**1,2,4-Triazine** (**7**).—Carboxylic acid hydrate (**6**) (200 mg) (1.4 mmoles) was heated at 120° in a Pyrex tube, sealed on one end, for 5 min. The pyrolysis product was washed with a total of 5 ml of chloroform. Vpc analysis of this solution indicated the presence of approximately equal amounts of water and the triazine. The chloroform washings were dried over anhydrous sodium sulfate, filtered, and evaporated to a volume of 1 ml by carefully blowing dry $N_2$ gas over the solution. The remaining yellow solution was chromatographed by preparative gas chromatography (8-ft silicone gum rubber (10%) on Diatoport S, injection port temperature 200°, column temperature 145°, helium flow rate 150 cc/min). The collected pale yellow oil which gradually solidified (mp 16–17.5°) weighed 46 mg (40% of theory): bp 156 (740 mm) (capillary); $n^{25}{}_{D}$ 1.5149.

*Anal.* Calcd for $C_3H_3N_3$: C, 44.42; H, 3.76; N, 51.82; mol wt, 81.1. Found: C, 44.65; H, 3.40; N, 51.55; mol wt, 85 (osmometric in benzene).

**3-D-1,2,4-Triazine** (**9**).—Carboxylic acid **6** (100 mg) was suspended in 15 ml of 98% $D_2O$, and the suspension was allowed to stand at room temperature, with occasional swirling, for 24 hrs. The carboxylic acid was then recovered by removal of the $D_2O$ by freeze-drying. The deuterated carboxylic acid **8** was then decarboxylated as described for the preparation of 1,2,4-triazine (**7**) to yield 25 mg of 3-D-1,2,4-triazine. The nmr spectrum of this compound is recorded in Table I.

**Acknowledgment.**—The partial financial support of this work by the National Science Foundation in the form of a Cooperative Graduate Fellowship to J. M. B. is gratefully acknowledged.

---

# The Structure of 2-Pyrazolin-5-one Dyes

HEINOSUKE YASUDA AND HIROSHI MIDORIKAWA

*The Institute of Physical and Chemical Research, Komagome, Tokyo, Japan*

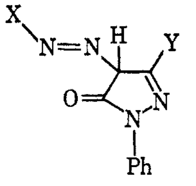
*Received August 10, 1965*

2-Pyrazolin-5-one dyes obtained by the coupling reaction of 1,3-diphenyl-2-pyrazolin-5-one with diazotized anilines exist in the solid state and in solutions as a strongly chelated hydrazone keto structure, IIIb, on the basis of results obtained by the nmr, infrared, and electronic spectral data.

The problem of the tautomeric structure of 4-arylazo-5-one dyes has been source of controversy for a long period. Recently, three groups of investigators have formulated "1-phenyl-3-methyl-4-phenylazo-2-pyrazolin-5-one" as Ia,[1] IIa,[2] and IIIa[3] on the basis of spectroscopic studies. Katritzky and Maine[4] have found that the 4-unsubstituted 2-pyrazolin-5-ones exist as tautomeric mixtures of the 2H and 4H isomers, and the 2H azo keto form (IV), accordingly, may also be considered for these dyes.

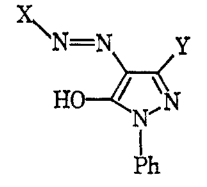
In the present work, the tautomeric structure of "1,3-diphenyl-4-arylazo-2-pyrazolin-5-ones" has been found to be the chelated hydrazone keto form (IIIb), corresponding to that assigned to the 3-methyl derivatives by Jones, *et al.*[3]

**Nmr Evidence.**—The nmr spectrum of the 1,3-diphenyl compound (Va) contained only peaks for aryl protons ($\delta = 7.34$ ppm) and a highly deshielded proton ($\delta = 13.89$ ppm); there was no signal in the 6.4-ppm region[5] corresponding to a proton at C-4. The low-field signal is in a position previously observed for hydrogen-bonded N–H peaks[6] and corresponds closely to the peak at 13.8–14.2 ppm found in the 3-methyl



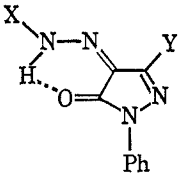
I

Ia, X = Ph; Y = Me
b, X = Ar; Y = Ph



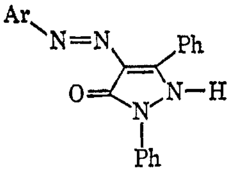
II

IIa, X = Ph; Y = Me
b, X = Ar; Y = Ph



III

IIIa, X = Ph; Y = Me
b, X = Ar; Y = Ph



IV

---

[1] F. A. Snavely, W. S. Trahanovsky, and F. H. Suydam, *J. Org. Chem.*, **27**, 994 (1962).

[2] W. Pelz, W. Puschel, H. Schellenberger, and K. Loffler, *Angew. Chem.*, **72**, 967 (1960).

[3] R. Jones, A. J. Ryan, S. Sternhell, and S. E. Wright, *Tetrahedron*, **19**, 1497 (1963).

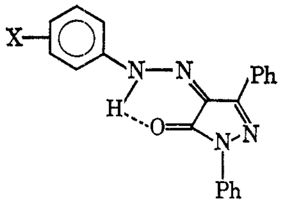
[4] A. R. Katritzky and F. W. Maine, *ibid.*, **20**, 299 (1964).

[5] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965).

[6] G. O. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).

TABLE I

PHYSICAL PROPERTIES OF 1,3-DIPHENYL-2-PYRAZOLIN-5-ONE DYES INVESTIGATED



| Compd | Substituent X | Mp, °C | Lit.[a] mp, °C | $\lambda_{max}$ | Log $\epsilon$ | $\lambda_{max}$ | Log $\epsilon$ | Cyclic C=O, cm$^{-1}$[b] KBr disk | Chloroform soln |
|---|---|---|---|---|---|---|---|---|---|
| Va | H | 170–171 | 171 | | | | | 1658 | 1658 |
| Vb | 2-Methyl | 176–177 | 183 | 265[c] | 4.44 | 414 | 4.41 | 1658 | 1658 |
| | | | | 263[d] | 4.54 | 414 | 4.49 | | |
| | | | | 263[e] | 4.45 | 412 | 4.43 | | |
| Vc | 3-Methyl | 168–169 | 179 | | | | | 1667 | 1664 |
| Vd | 4-Methyl | 185–186 | 193 | 268[c] | 4.52 | 417 | 4.51 | 1658 | 1660 |
| | | | | 266[d] | 4.63 | 414 | 4.59 | | |
| | | | | 265[e] | 4.38 | 410 | 4.55 | | |
| Ve | 2-Methoxy | 139–140[f] | | 269[c] | 4.41 | 429 | 4.37 | 1667 | 1664 |
| | | | | 267[d] | 4.43 | 427 | 4.37 | | |
| | | | | 267[e] | 4.49 | 417 | 4.43 | | |
| Vf | 4-Methoxy | 160–161 | 167 | 274[c] | 4.42 | 433 | 4.40 | 1658 | 1656 |
| | | | | 272[d] | 4.53 | 430 | 4.40 | | |
| | | | | 270[e] | 4.59 | 424 | 4.55 | | |
| Vg | 2-Ethoxy | 196–197 | 206 | | | | | 1667 | 1661 |
| Vh | 2-Chloro | 170–171 | 177 | 268[c] | 4.42 | 409 | 4.39 | 1669 | 1667 |
| | | | | 266[d] | 4.61 | 407 | 4.56 | | |
| | | | | 266[e] | 4.36 | 404 | 4.31 | | |
| Vi | 3-Chloro | 186–187 | 193 | | | | | 1669 | 1667 |
| Vj | 4-Chloro | 205–206 | 216 | 266[c] | 4.50 | 411 | 4.53 | 1659 | 1662 |
| | | | | 265[d] | 4.51 | 408 | 4.51 | | |
| | | | | 265[e] | 4.42 | 408 | 4.42 | | |
| Vk | 2-Nitro | 194–195 | 204 | | | | | 1678 | 1681 |
| Vl | 4-Nitro | 232–233 | 245 | | | | | 1672 | 1672 |
| Vm | 4-*n*-Butoxycarbonyl | 164–165[g] | | | | | | 1667 | 1664 |
| Vn | 2-Methoxycarbonyl | 176–177[h] | | | | | | 1680 | 1672 |

[a] D. D. M. Casoni, *Boll. Sci. Fac. Chim. Ind. Bologna*, **9**, 4 (1951). [b] All have strong intensity. [c] In chloroform solution. [d] In 99% ethanol solution. [e] In *n*-hexane solution. [f] *Anal.* Calcd for $C_{22}H_{18}O_2N_4$: C, 71.33; H, 4.90; N, 15.13. Found: C, 71.00; H, 4.77; N, 15.31. [g] *Anal.* Calcd for $C_{26}H_{24}O_3N_4$: C, 70.89; H, 5.49; N, 12.72. Found: C, 70.63; H, 5.18; N, 12.89. [h] *Anal.* Calcd for $C_{23}H_{18}O_3N_4$: C, 69.33; H, 4.55; N, 14.06. Found: C, 68.96; H, 4.41; N, 14.25.

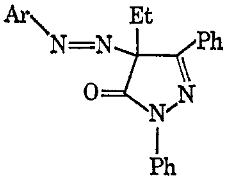
series.[3] More definite evidence for the location of the deshielded proton observed may be adduced from the infrared studies discussed later; *i.e.*, the absence of enolic hydroyl is confirmed.

Thus, the evidence presented in this nmr spectrum of Va favors the IIIb or IV form. The infrared and electronic spectra cannot be interpreted in terms of the tautomeric structure such as IV, but they appear compatible with the hydrazone keto form such as IIIb.

**Infrared Spectra.**—The "1,3-diphenyl-4-arylazo-2-pyrazolin-5-ones" investigated have a strong perpendicular band near 1660 cm$^{-1}$ attributable to the cyclic C=O frequency[1,7–9] in the solid state and in chloroform solution (see Table I). The 1,3-diphenyl compounds concerned may, therefore, be expected to have no tautomeric form IIb. The 1,3-diphenyl derivatives studied, on the other hand, do not reveal a band above 3100 cm$^{-1}$ assignable to the nitrogen–hydrogen bond[10–13] in the solid state and in solutions.

The perpendicular band near 1550 cm$^{-1}$ observed in all 2-pyrazolin-5-one dyes examined resembles very closely the N=N vibration found by Snavely, *et al.*[1] Bassignana and Cogrossi[14] have recently examined the spectra of over one hundred azo compounds and assigned the band near 1570 cm$^{-1}$ to the aromatic ring skeletal C=C vibration conjugated with a N=N grouping, and the two bands near 1410 and 1145 cm$^{-1}$ to the N=N vibration.

Nevertheless, in the spectra of 1,3-diphenyl-4-ethyl-4-arylazo-2-pyrazolin-5-ones (VI), which are closely



VI, Ar
a, H
b, 4-Cl
c, 4-Me
d, 4-OMe

---

(7) P. E. Gagnon, J. L. Boivin, and R. N. Jones, *Can. J. Res.*, **B27**, 190 (1949).

(8) P. E. Gagnon, J. L. Boivin, and R. J. Paquin, *Can. J. Chem.*, **31**, 1025 (1953).

(9) H. Yasuda, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **56**, 267 (1962).

(10) S. E. Darmon and G. B. B. M. Sutherland, *Nature*, **164**, 440 (1949).

(11) M. Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215 (1949).

(12) S. E. Darmon, *Discussions Faraday Soc.*, **9**, 325 (1950).

(13) W. Klemperer, M. W. Cronyn, A. H. Maki, and G. C. Pimental, *J. Am. Chem. Soc.*, **76**, 5846 (1954).

(14) P. Bassignana and C. Cogrossi, *Tetrahedron*, **20**, 2361 (1964).

analogous to the tautomeric form Ib, the band near 1550 cm$^{-1}$ definitely vanishes in the solid state and in chloroform solution.

From the results obtained above, the 1550-cm$^{-1}$ band observed must be assigned not to an C=C–N=N– grouping, but to the vibration of the C=C–NH–N= (not cyclic) system. This system is supported by the nmr spectrum discussed above.

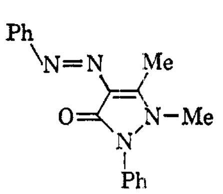
In consequence, the tautomeric structure IIIb for the 1,3-diphenyl-2-pyrazolin-5-one dyes investigated is the only one which accomodates these observations.

**Electronic Spectra.**—The 2-pyrazolin-5-one dyes examined can be described as having the chelated IIIb structure from the nmr and infrared studies. This problem was investigated further on the basis of the electronic spectra.

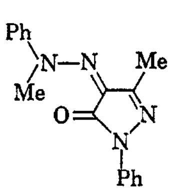
Pelz, *et al.*,[2] have studied the spectra of "1-phenyl-3-methyl-4-phenylazo-2-pyrazolin-5-one" and the corresponding O-methyl derivative; they have assigned this azo compound to the azo enol form, which corresponds to the tautomeric form IIb. This assignment is now believed to be incorrect, for the absence of enolic hydroxyl is confirmed by a study of the infrared spectra.

Burawoy, *et al.*,[15] who have investigated the electronic spectra of 2-phenylazo-1-naphthol and related compounds, have shown that the 1-naphthol exists in a solution as 1,2-naphthoquinone-2-phenylhydrazone; the spectrum of the 1-naphthol is very different from that of the corresponding O-methyl derivative, but it is almost identical with that of its N-methyl derivative.

From this point of view, it seems that it would be of interest to compare the electronic spectra of "1,3-diphenyl-4-phenylazo-2-pyrazolin-5-one" (Va) and its 4-ethyl derivative (VIa), which very closely resembles the tautomeric form Ib. Furthermore, 1-phenyl-2,3-dimethyl-4-phenylazo-3-pyrazolin-5-one (VII)[16] and N-methyl-1-phenyl-3-methyl-4-phenylhydrazono-2-pyrazolin-5-one (VIII),[1] which are closely analogous to the tautomeric structures, IIIb and IV, were also examined.



VII



VIII

The spectra of the two compounds, Va and VIII, in ethanol solution show similar absorptions, whereas the absorption curve of Va is not identical with those observed for the compounds VIa and VII, respectively. Thus, the close similarity between the absorption curves of Va and VIII would appear to work against the formulation of the 2-pyrazolin-5-one dyes examined as the hydrazone keto form IIIb.

On the other hand, Burawoy, *et al.*,[15] have confirmed that, in arylazonaphthols, the concentration of hydrazone–quinone tautomers increases in the order of substituents, 4-OMe < 4-OMe-3,5-diMe < H < 3-OMe < 2-OMe, 4-Me < 3-Me < H < 2-Me and 4-Cl < 3-Cl < 2-Cl, and in the order of solvents, *n*-hexane < ethanol < chloroform.

This interpretation was applied to the absorption spectra of the 2-pyrazolin-5-one dyes, in which anisyl-, tolyl-, and chlorophenylhydrazono substitute in the 4-position in *n*-hexane, ethanol, and chloroform solutions. The data obtained are collected in Table I.

It should be noted that the long-wave bands of all the dyes measured undergo a hypsochromic shift with a decrease in the dielectric constant of the solvent, but these are smaller hypsochromic effect in short-wave bands, as shown in Table I. Furthermore, a comparison of the three pairs of dyes, Vf and Ve, Vd and Vb, and Vj and Vh, in each solvent shows that the relationship between 4- and 2-substituents produces only very small changes in the values of $\lambda_{max}$ and log $\epsilon$ for the short- and long-wave bands, and within each pair the absorption bands are to be expected on the basis of solvent and substituent effects; accordingly, the small spectral changes do not afford a measure of the tautomeric equilibrium. It seems desirable, however, to confirm the equilibrium process by a p$K_a$ value.

## Experimental Section[17]

**Spectral Measurements.**—The nmr spectra were obtained at 40 Mc on a (JNM-H-40) high-resolution nmr spectrometer. Tetramethylsilane was used as the internal standard, and all chemical shifts were given in parts per million downfield from this origin. The spectra were calibrated by interpolation from side bands generated by an audio oscillator, and were made in deuteriochloroform solution containing *ca.* 10% by weight of solute.

The infrared spectra were recorded with a Nippon Bunko DS-201 infrared spectrophotometer and a Shimazu IR-27-C infrared spectrophotometer, fitted with sodium chloride prism, in KBr disk and chloroform solution. A calibration spectrum of polystyrene film was superimposed on each chart.

The electronic spectra were measured with a Cary Model 14 recording spectrophotometer with 1-cm quartz cells. Absolute ethanol, chloroform, and *n*-hexane were used as solvents.

**Preparation of 1,3-Diphenyl-4-arylhydrazono-2-pyrazolin-5-ones (Va–n).**—These compounds were prepared by coupling of the appropriate diazotized anilines to 1,3-diphenyl-2-pyrazolin-5-one,[18] according to the procedure described below.

**Diazotization. Method A.**—The aniline (0.0025 mole) was dissolved in diluted hydrochloric acid (2 ml in 10 ml of water) and diazotized with sodium nitrite solution (0.25 g in 5 ml of water) below 5° with hand stirring.

**Method B.**—The aniline (0.0025 mole) was dissolved in hot acetic acid (5 ml) containing concentrated hydrochloric acid (2 ml). To this acidic solution, on cooling, was added sodium nitrite (0.25 g) in small portions below 5° with mechanical stirring.

**Coupling Reaction.**—A solution of 2-pyrazolin-5-one (0.59 g, 0.0025 mole) in hot acetone (30 ml) containing crystalline sodium acetate (2 g) was diluted with water (30 ml) and cooled below 10°. A diazonium solution was then added slowly with mechanical stirring. During the addition, a colored solid separated. The resulting dye was collected, washed with diluted methanol, and recrystallized from suitable solvents. The results obtained are listed in Table I.

**Preparation of 1,3-Diphenyl-4-ethyl-4-arylazo-2-pyrazolin-5-ones (VIa–d).**—These compounds were synthesized by coupling the appropriate diazotized anilines to 1,3-diphenyl-4-ethyl-2-pyrazolin-5-one.[8] An appropriate aniline (0.01 mole) was dissolved in diluted hydrochloric acid (3 ml in 2 ml of water), and diazotized with sodium nitrite solution (0.69 g in 2 ml of water) below 5°. To a solution of the 4-ethylpyrazolinone (2.6 g) in 50% methanol (50 ml) buffered with crystalline sodium acetate (5 g) was added the diazotized solution. The coupling mixture

---

(15) A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952); A. Burawoy, and A. R. Thompson, *ibid.*, 1443 (1953).

(16) A. Michaelis and H. Schlecht, *Ber.*, **39**, 1954 (1906).

(17) All melting points are uncorrected.

(18) L. Knorr and C. Klotz, *Ber.*, **20**, 2545 (1887).

was diluted with water, and a colored product which separated was collected and recrystallized from ethanol–water.

**The 4-phenylazo derivative (VIa)**: yellow needles, mp 99–100°, lit.[2] 96°. *Anal.* Calcd for $C_{23}H_{20}ON_4$: N, 15.21. Found: N, 15.02.

**The 4-(*p*-chlorophenylazo) derivative (VIb)**: yellow needles, mp 97–98° (dec). *Anal.* Calcd for $C_{23}H_{19}OClN_4$: N, 13.91. Found: N, 13.55.

**The 4-(*p*-tolyl) derivative (VIc)**: yellow needles, mp 88–89° (dec). *Anal.* Calcd for $C_{24}H_{22}ON_4$: N, 14.65. Found: N, 14.57.

**The 4-(*p*-anisyl) derivative (VId)**: yellow needles, mp 79–80° (dec). *Anal.* Calcd for $C_{24}H_{22}O_2N_4$: N, 14.06. Found: N, 13.92.

**Acknowledgment.**—The authors wish to thank Professor Taro Hayashi of Ochanomizu University and Professor Tatsuo Takeshima of Shizuoka University for their interest and suggestions. We are also indebted to Dr. H. Homma and his staff for the microanalyses.

---

# The Nature of the Alkali-Induced Isomerization of 2,3,4,4a,6,6a-Hexahydro-6aα-hydroxy-4aβ,6β,7,9-tetramethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene

D. S. DEORHA[1] AND PADMA GUPTA

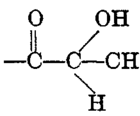
*Department of Chemistry, University of Rajasthan, Jaipur, India*

*Received November 9, 1965*

The base-catalyzed isomerization of the hydroxypentalene (III, R = H) appears to involve epimerization at the starred carbon atom. The view is substantiated by the fact that the γ-hydroxy acid (X, R = $R_1$ = H), derived from acid hydrolysis of carbethoxymethylhydroxypentalene (X, R = H, $R_1$ = $C_2H_5$), is converted to the γ-lactone (XII) on being heated with alkali and subsequent acidification. Structures III (R = H) and VIII (R = H), previously suggested for the hydroxypentalene and its alkali isomerized product, are confirmed by obtaining their methyl ethers from γ-hydroxy acid (X, R = $R_1$ = H) and the γ-lactone (XII), respectively, after subjecting these to appropriate reactions.

Ozonolysis[2a] of the grisene (I) (Chart I) in methyl acetate provided a product of structure II (R = $CH_3$) while oxidation of the former by osmium tetroxide furnished an alcohol (II, R = H). The later could be methylated to yield a product, identical with the former (II, R = $CH_3$). These oxidation products (II, R = $CH_3$, and II, R = H) were assigned[2b] configurations III (R = $CH_3$) and III (R = H), respectively. Dean, *et al.*,[2b] found that while the latter III (R = H) isomerized in warm alkali, the former (III, R = $CH_3$) was unaffected. This suggested that the hydroxyl group must be essential for this change. The new isomer gave a methyl ether different from but isomeric with the ozonolysis product (III, R = $CH_3$) and was so closely similar to the original alcohol (III, R = H) both in chemical and spectroscopic properties that the change was considered stereochemical rather than structural in origin. The view was substantiated and the center involved shown to be that starred in III (R = H) by the fact that neither compound IV nor V was affected by alkali.

An explanation[2b] of the above results was provided by the suggestion that bases would induce β elimination, thus reversing the cyclization which gave ring B of the alcohol (III, R = H). In the resulting glycol (VI, R = H), however, the presence of the tertiary alcoholic group allows a reverse aldol condensation so as to open the remaining heterocyclic ring generating, if only momentarily, an intermediate (VII). This is obviously not likely in compound VI (R = $CH_3$). There is now present a grouping



$$-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{OH}{\underset{H}{C}}-CH_3$$

in VII well known to be epimerizable by bases, so that, when the rings close again by reversal of the sequence, the more stable of the two structures (III, R = H, and VIII, R = H) would be favored. The benzene ring eclipses the methyl group at the atom starred in III (R = H) but the resulting repulsion is absent from the epimer (VIII, R = H), so that with VIII (R = H) as the structure of the new isomer, all the facts are satisfactorily explained.

That the isomerization of the alcohol (III, R = H) by alkali is due to the change in the position of methyl group at the starred carbon atom has now been demonstrated. The grisene[3] (IX) on oxidation by osmium tetroxide furnished a product which was similar in spectroscopic properties to the alcohol (III, R = H). By analogy with arguments used for assigning the configuration of dibenzopentalene (II, R = H) as III (R = H), the oxidation product of the grisene (IX) may have the configuration as in X (R = H; $R_1$ = $C_2H_5$).

On hydrolysis with sulfuric acid dihydrate, the difuranoid compound (X, R = H; $R_1$ = $C_2H_5$) yielded an acid (X, R = $R_1$ = H) indicating that OH and $CH_2COOH$ in it do not exist on the same side of ring B. Had the two groups been in *cis* configuration, lactonization to form a γ-lactone would have been spontaneous. However, when the acid (X, R = $R_1$ = H) was warmed with alkali, acidification furnished a neutral solid showing infrared characteristics of a γ-lactone. This is possible only when alkali induces epimerization at the center starred in the acid (X) to place the $-CH_2COOH$ group on the side of the OH group with an opportunity for γ-lactonization. All attempts to obtain the acid (XI, R = $R_1$ = H) have been unsuccessful. The identical γ-lactone (XII) was obtained from the alkaline hydrolysis of compound X (R = H; $R_1$ = $C_2H_5$), followed by acidifica-

---

(1) Deceased.

(2) (a) F. M. Dean, T. Francis, and K. Manunapichu, *J. Chem. Soc.*, 4551 (1958); (b) F. M. Dean, D. S. Deorha, J. C. Knight, and T. Francis, *ibid.*, 327 (1961).

(3) D. S. Deorha, unpublished work.