TABLE II

$k_4/k_2$ IN NEUTRAL AND ACID SOLUTIONS.

Dose rate 1000 was r. min.$^{-1}$; total dose was 4000 r.

| Solute and its concn. $M$ | | | Neutral solutions | | | Acid solution |
|---|---|---|---|---|---|---|
| | | $C_{Fe(CN)_6^{-3}}$, $M$ | Electron scavenger present $M$ | $G_{hydrogen}$ | $k_4/k_2$ | $k_4/k_2$[12] |
| Glucose | 0.01 | $1.5 \times 10^{-4}$ | 0.05 bicarbonate | 0.71 | 108 | 100 |
| Glucose | .01 | $8 \times 10^{-5}$[a] | 0.05 bicarbonate | .86 | 75 | |
| Glycerol | .01 | $7.5 \times 10^{-5}$[a] | 0.05 bicarbonate | .80 | 128 | 200 |
| Methanol | .10 | $6.2 \times 10^{-5}$[a] | 0.05 bicarbonate | .81 | 1500 | 2350 |
| 2-Propanol[b] | .05 | $9.3 \times 10^{-4}$ | $9.3 \times 10^{-4}$ ferricyanide | .82 | 39 | 77 |
| Formate | .047 | $3.14 \times 10^{-3}$ | $2 \times 10^{-4}$ acetone | .75 | 18 | 15.4 |

[a] Corrections have been made for the amount of ferricyanide which disappears during the irradiation. [b] In the presence of $10^{-4}$ $M$ $Na_2HPO_4$.

These reactions of $e_{aq}$ to produce $H_2$ as a final product in neutral solutions are relatively slow. Thus, minute quantities of electron scavengers which may be impurities, or products of irradiation will influence the values of $G_{hydrogen}$ when $G_{hydrogen} > 1.1$. The hydrogen yields obtained in the absence of an appropriate electron scavenger have no quantitative meaning.

When a sufficient amount of an electron scavenger is present, the hydrogen yield equals the sum of $G_{H_2} + G_3$ (where $G_{H_2}$ denotes the so called "molecular" yield of hydrogen). $G_3$ seems to be constant and its value is $0.55 \pm 0.05$ in all the above systems, assuming $G_{H_2} = 0.5$. Since $G_{H_2}$ may differ somewhat from this value and depend on the solute and on its concentration,[11] the sum of $G_{H_2} + G_3$ is expected to vary to the same extent.

To test whether the assumed reaction (3) really produces H atoms as such, competition between ferricyanide and $RH_2$ was carried out. Ferricyanide reacts with H atoms according to

$$H + Fe(CN)_6^{-3} \longrightarrow H^+ + Fe(CN)_6^{-4} \quad (4)$$

The yield of $H_2$ may be used to determine $k_4/k_2$, at neutral pH.

In Table II we compare the $k_4/k_2$ values, obtained by the competition of ferricyanide and $RH_2$ for H atoms produced in neutral solutions in the presence of a sufficient amount of an electron scavenger, to those obtained for acid solutions.[12]

The $G_{hydrogen}$ values are accurate to ± 5%. The values of $k_4/k_2$ were calculated assuming that $G_{H_2} = 0.5$ in all cases. From this $G_3 = 0.55$ results.

The agreement between the acid and neutral $k_4/k_2$ values confirms that at neutral pH the acid form of H atoms is produced by a mechanism which does not involve reactions of the neutral form of the reducing radicals in the bulk.

At present we have no explanation for the results[7,8] in systems where $G_3 \leq 0.30$. However, in our systems, the measure of $G_3$ is direct, the only assumption being the value of the "molecular" hydrogen yield.

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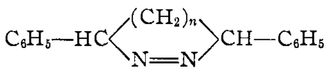
[11] H. A. Schwarz, *J. Am. Chem. Soc.*, **77**, 4960 (1955).

[12] J. Rabani, *J. Phys. Chem.*, **65**, 361 (1961).

## A FIVE-MEMBERED RING AZO COMPOUND. A STEREOSELECTIVE DECOMPOSITION

*Sir:*

Recently increased impetus has been given to the question of whether or not biradicals couple with retention of configuration. Overberger and co-workers[1,2] have studied the decomposition of the seven- and eight-membered ring azo compounds of type I. One isomer of the seven-membered ring azo compound (I, $n = 3$) was decomposed at 80 and 100° to give 1,5-diphenyl-1-pentene and a mixture of *cis*- and *trans*-1,2-diphenylcyclopentanes. One isomer of the eight-membered ring azo compound (I, $n = 4$) required somewhat higher temperatures (about 145°) but again, the corresponding olefin and a mixture of *cis*- and *trans*-1,2-diphenylcyclohexanes were obtained. Rinehart and Van Auken[3] have shown that at low temperatures, the photolysis of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline and of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline gave the corresponding cyclopropanes with retained configuration. Jones[4] also has studied the stereochemistry of the decomposition of 2-pyrazolines and found that the configuration of the resulting cyclopropanes does not depend upon their stability but rather upon the configuration of the intermediate 1-pyrazolines.



I

We wish now to report the synthesis and the stereospecific decomposition of the five-membered ring azo compound 3,5-diphenyl-1-pyrazoline (Ia), an analog of I ($n = 1$). Compound Ia was prepared by the addition of styrene to phenyldiazomethane. It is a white crystalline solid, m.p. 109–110° (dec.), $\lambda_{max}^{EtOH}$ 329 m$\mu$, $\epsilon_{max}$ 291.

*Anal.* Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35. Found: C, 81.04; H, 6.28.

Two products could arise from the addition of styrene to phenyldiazomethane. Evidence for structure Ia was obtained as described.

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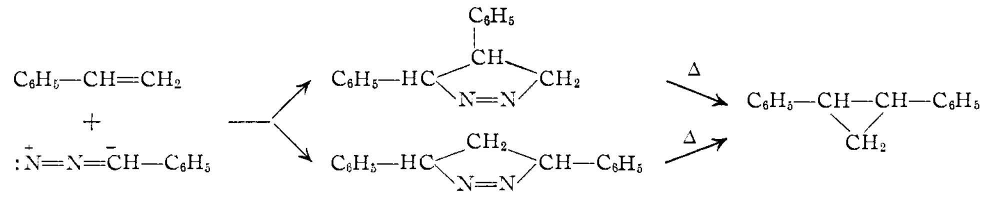
[1] C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 2317 (1958).

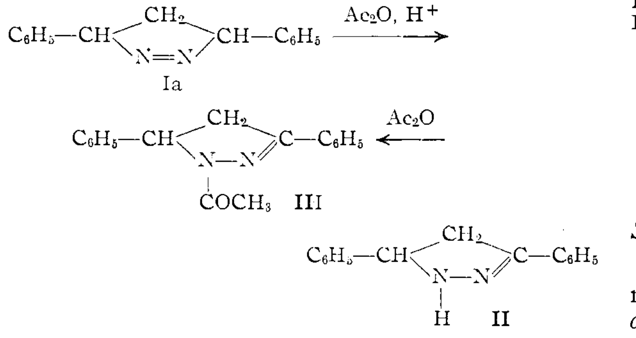
[2] C. G. Overberger and I. Tashlick, *ibid.*, **81**, 217 (1959).

[3] K. L. Rinehart and T. V. Van Auken, *ibid.*, **82**, 5251 (1960).

[4] W. M. Jones, *ibid.*, **82**, 3136 (1960).



The reaction of Ia with acetic anhydride in the presence of a catalytic amount of *p*-toluenesulfonic acid gave 1-acetyl-3,5-diphenyl-2-pyrazoline (III), m.p. 125–125.5°, identical (infrared spectra and mixed melting point) with an authentic sample prepared by the reaction of acetic anhydride with II.[5a,b] Compound Ia is the first stable 1-pyrazoline[6] having an $\alpha$-hydrogen capable of isomerizing to a conjugated system. This type of 1-pyrazoline usually rearranges spontaneously to a 2-pyrazoline under conditions of their synthesis. The isomerization of Ia to II in dilute ethanolic hydrochloric acid was followed spectrophotometrically by the appearance of the hydrazone peak at 291 m$\mu$.



Thermal decomposition of Ia, presumably a mixture of the D,L-*trans*-isomers at 70°, resulted in only one product, *trans* 1,2-diphenylcyclopropane[7] (D,L pair), $n^{25}_D$ 1.5951 ($n^{20}_D$ 1.5995, prepared by base catalyzed decomposition of the corresponding 2-pyrazoline[8]) in contrast to the nonselectivity exhibited by the seven- and eight-membered ring compounds (I, $n$ = 3, 4). Photochemical decomposition in hexane solution at 25° also gave this same selectivity. One explanation may be that there is much less time for the radicals to become relatively free in the formation of the cyclopropane than in the case of formation of the cyclopentane or the cyclohexane. This might be due to the closer proximity of the two radicals in the five-membered ring case. We can safely discount the possibility that the five-membered ring azo compound is the *cis* isomer and that the formation of the *trans* cyclopropane represents the formation of the most stable isomer since the base catalyzed decomposition of 3,5-diphenyl-2-pyrazoline (II) at 200° gave both *cis*- and *trans*-1,2-diphenylcyclopropanes (about 50:50 mixture) as was shown by Curtin, *et al.*,[8] and checked by us.

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[5] (a) S. G. Beech, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, 4684 (1952). (b) M. Hamada, *Botyu Kagaku*, **21**, 22 (1956).

[6] Smith and co-workers, *J. Am. Chem. Soc.*, **65**, 159 (1943), claimed to have isolated some 1-pyrazolines but these claims have not been substantiated by any data.

[7] The n.m.r. spectrum clearly shows that the *trans* isomer is the only product formed and was identical with that reported in reference 8.

[8] D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

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## INHERENTLY DISSYMETRIC CHROMOPHORES. OPTICAL ROTATORY DISPERSION OF $\alpha,\beta$-UNSATURATED KETONES AND CONFORMATIONAL ANALYSIS OF CYCLOHEXENONES[1,2]

*Sir:*

Derivation of the octant rule[3] for the 290 m$\mu$ n-$\pi^*$ transition of saturated ketones rests, *inter alia*, on the local symmetry of the carbonyl chromophore which exhibits two orthogonal reflection planes. In $\alpha,\beta$-unsaturated ketones, one or both of these planes is lost and hence the octant rule is in general no longer applicable.

This reduction in local symmetry can be turned to advantage if one shifts attention from the n-$\pi^*$ to the shorter wave length $\pi$-$\pi^*$ transition of the $C=C-C=O$ grouping, which, if nonplanar, may be regarded as an inherently dissymmetric chromophore.[4,5] Because of the similarity in the $\pi$-systems of $C=C-C=O$ and $C=C-C=C$, the helicity rule for cisoid dienes[6] is expected to apply also to $\alpha,\beta$-unsaturated ketones. Calculations utilizing simple Hückel type wave functions bear out this point: cisoid conformation A and transoid conformation B are to be associated with a positive Cotton effect centered at the wave length corresponding to the K-band, *i.e.*, the lowest $\pi$-$\pi^*$ transition near 240–260 m$\mu$, while a negative Cotton effect would be exhibited by their mirror-image representations. For sufficiently large angles of skew, the rotational strengths of the $\pi$-$\pi^*$ transitions of the above discussed inherently dissymmetric chromophore will be an order of magni-

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[1] "Optical Rotatory Dispersion Studies." LXXII. For paper LXXI, see C. S. Barnes and C. Djerassi, *J. Am. Chem. Soc.*, **84**, in press (1962).

[2] Financial support by the Alfred P. Sloan Foundation (K. M.) and by the National Science Foundation (grants No. G15746 and G-19905) is gratefully acknowledged.

[3] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[4] A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

[5] A. Moscowitz, K. Mislow, M. A. W. Glass and C. Djerassi, *J. Am. Chem. Soc.*, in press; K. Mislow and J. G. Berger, *ibid.*, in press; K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *ibid.*, in press.

[6] A. Moscowitz, E. Charney, U. Weiss and H. Ziffer, *J. Am. Chem. Soc.*, **83**, 4661 (1961).