

S-protein and that apparently no direct function in the catalytic mechanism of RNase can be ascribed to it. This is in agreement with the previous conclusions of Richards and Vithayathil,¹¹ based on observations with methionine-13 modified S-peptide, and also with those of Potts, *et al.*,¹⁴ but it appears to disagree with the conclusions of Hofmann, *et al.*, based on their observations with the oxidized synthetic tridecapeptide.²

The interesting implications of the effect of alkali on the activity of C-peptide are under investigation.

BIOCHEMISTRY DIVISION
DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

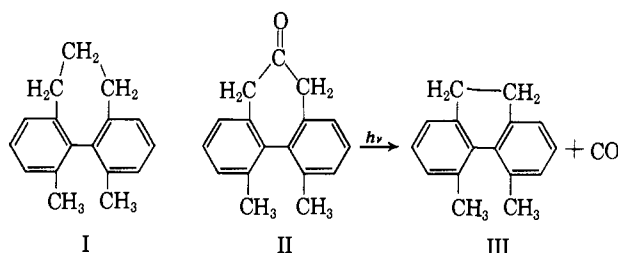
J. M. PARKS
M. B. BARANCIK
FINN WOLD

RECEIVED JULY 8, 1963

Photoracemization of Biphenyls

Sir:

Among the many photochemical isomerizations which have been studied to date,¹ there appears to be no instance of a transformation whose mechanism does not require bond breaking and bond reformation. We now report the photoracemization of hydrocarbon I as the first example of a light-induced interconversion of conformational stereoisomers.



Hydrocarbon I² may be racemized by heating in the dark above 200° (E_{act} 39 kcal./mole). Irradiation (Hanovia high-pressure quartz mercury-vapor lamp, 450 w.) of 0.1–0.2% solutions in ether under nitrogen at 23–25° results in racemization, with initial half-lives varying from 4 to 30 hr.³ The process appears to be singularly uncomplicated by side reactions. The interposition of a Pyrex shield between the lamp and the solution arrests the racemization; I has λ_{max} 240 m μ ($\log \epsilon$ 4.06)² and does not absorb significantly above 260 m μ .

Our results may be interpreted most economically by postulating that absorption of energy near 240 m μ (119 kcal./mole) is followed by internal conversion of the initially formed electronically excited molecule to the vibrationally excited "hot" ground state molecule⁴ which is directly produced in the classical thermal racemization.⁵

We have also found that ketone II² undergoes simultaneous racemization and decarbonylation under the conditions stated. In a typical experiment, irradiation

of II ($[\alpha]_D - 635^\circ$, benzene) for 6 hr. gave 21% of II ($[\alpha]_D - 582^\circ$) and 43% of III ($[\alpha]_D + 194^\circ$, benzene), identified by infrared, g.l.c., and rate constant of racemization.⁶

Interposition of a Pyrex shield does not substantially alter these results. In a typical experiment, irradiation of II ($[\alpha]_D - 620^\circ$) for 6 hr. gave 34% of II ($[\alpha]_D - 580^\circ$) and 32% of III ($[\alpha]_D + 242^\circ$). The last finding is not unexpected, since we have previously recognized the spectroscopic interaction of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in II² and have looked upon the whole molecule as an extended dissymmetric chromophore.⁷ It is surprising, however, that the decarbonylation reaction is 4–5 times as important (in terms of product yield) as racemization. Absorption of radiation at 300 m μ (95 kcal./mole) is more than sufficient to supply the energy required to racemize II (E_{act} 36 kcal./mole), yet degradation of the electronically excited molecule *via* bond cleavage is the preferred pathway.⁸

Compound II is the dibenzo derivative of 3,5-cycloheptadienone, a compound which has never been obtained in optically active form but which has been photochemically decarbonylated⁹ to a mixture of isomeric 1,3,5-hexatrienes.¹⁰ We stress that in II and in 3,5-cycloheptadienone, the interaction of the carbonyl group with each of the two benzene rings, respectively double bonds, is identical. Chapman, *et al.*, have attempted to rationalize the absence of light-induced valence tautomerization in 3,5-cycloheptadienones by claiming⁹ that "careful examination of the model [of 3,5-cycloheptadienone] shows that the π -orbital of one double bond and the carbonyl π -orbital are well situated for interaction. The remaining double bond is poorly situated for interaction with... the carbonyl." This statement is in error, since in actual fact the two double bonds are stereochemically and spectroscopically *completely equivalent*; as we have pointed out some time ago, the carbon–oxygen bond in systems of this type is coincident on a twofold symmetry axis.¹¹

We have extended the decarbonylation reaction to other systems (bisnor-II \rightarrow 9,10-dihydrophenanthrene, doubly bridged diketone¹² \rightarrow 4,5,9,10-tetrahydropyrene) but the synthetic usefulness is severely limited by the extensive formation of by-products (*inter alia*, the carbinols).

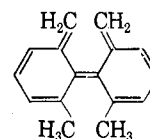
(6) K. Mislow and H. B. Hopps, *J. Am. Chem. Soc.*, **84**, 3018 (1962).

(7) A. Moscovitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

(8) Whatever the mechanism of the photochemical decarbonylation, we note that the possible intervention of long-lived diradical intermediates will not result in racemization since the blocking substituents ($\text{CH}_2\text{CO}^\cdot/\text{CH}_2^\cdot$ or $\text{CH}_2^\cdot/\text{CH}_2^\cdot$) remain.⁸

(9) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

(10) The corresponding product in our case would have the structure shown. However, we have no evidence for the intervention of such a reactive intermediate.



(11) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(12) K. Mislow, E. Simon, and H. B. Hopps, *Tetrahedron Letters*, **No. 22**, 1011 (1962).

(13) National Science Foundation Cooperative Predoctoral Fellow, 1963–1964.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK 53, NEW YORK

KURT MISLOW
ARNOLD J. GORDON¹³

RECEIVED SEPTEMBER 18, 1963

(1) *E.g.*, P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, **15**, 393 (1961); "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 367 ff.

(2) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

(3) The kinetic results of 15 runs were not quantitatively reproducible. The product of racemization (recovered in nearly quantitative yield) was identical (by infrared and g.l.c.) with starting I. In one experiment the hydrocarbon was racemized to the extent of 98–99%, initial $[\alpha]_D + 244^\circ$, final $[\alpha]_D + 4^\circ$ (benzene).

(4) A similar situation exists in conjugated dienes as has been pointed out by R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3982 (1962).

(5) Cleavage of bonds to benzyl carbon is not likely to result in racemization, since the resulting diradical is a dissymmetric tetrasubstituted unbridged biphenyl whose racemization energy barrier should greatly exceed that of I.