

COMMUNICATIONS TO THE EDITOR

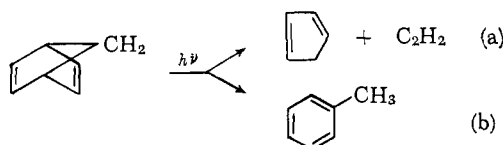
Photolysis of $\Delta^{2,5}$ -Bicyclo[2.2.1]heptadiene in the Vapor Phase

Sir:

Ultraviolet irradiation of $\Delta^{2,5}$ -bicyclo[2.2.1]heptadiene I (BCHD) in ether solution causes isomerization in 67% yield to the valence tautomeric quadricyclene II.¹ In an attempt to investigate the formation of



quadricyclene, BCHD was photolyzed in the vapor phase. We wish to report that in the vapor phase BCHD exhibited at least two primary processes, (a) decomposition to acetylene and cyclopentadiene and (b) isomerization to toluene. No valence tautomeric quadricyclene was detected.



Irradiation of BCHD with 2537-Å. radiation in a mercury-free system over the temperature range 25–50°, at initial pressures of 4–31 mm., produced acetylene and cyclopentadiene in equal amounts; toluene was a minor product. A low pressure Hg arc was used in conjunction with a Corning 7910 filter which eliminated radiation of shorter wave length. The photolysate was analyzed by gas chromatography using a 26-ft. silicone grease column (25% by wt. on Celite); individual components were collected as they were eluted from the column and each was identified mass spectrometrically. The identity of cyclopentadiene was also confirmed by ultraviolet absorption (λ_{\max} 2400 Å., ϵ 3000)²; the infrared spectrum of product cyclopentadiene was found to be identical with that in the literature.³ Toluene was identified in the gas chromatograph by its retention time in comparison with that of an authentic sample (Phillips research grade toluene). In addition to a silicone grease column, a 6-ft. Reoplex column (18% by wt. on Celite) and a 6-ft. Ucon column (16% by wt. on Celite) were used to detect quadricyclene but were unsuccessful.

Using acetone as internal actinometer, the intensity of light was found to be 4.21×10^{13} quanta/cc. sec. The quantum yields obtained are given in Table I.

TABLE I

P, mm.	Inert gas, mm.	$\Phi_{C_2H_2}$	$\Phi_{C_5H_6}$	$\Phi_{CH_3C_6H_5}$
4–31	Nil	0.49 \pm 0.03 ^a	0.50 \pm 0.03 ^a	0.056 \pm 0.013 ^a
12.8	H ₂ 300	0.50	0.49	0.048
12.5	H ₂ 690	0.45 ^b	0.42 ^b	0.040 ^b
12.0	He 650	0.42 ^c	0.41 ^c	0.050 ^c
12.0	ether sol.	0.12	0.14	0.042

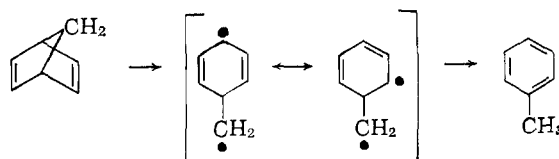
^a Average of 25 experiments. ^b Average of 5 experiments. ^c Average of 3 experiments.

It is quite evident from the data given in Table I that in the medium pressure range (300 mm.) the quan-

(1) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).(2) L. W. Pickett, E. Paddock, and E. Sackter, *J. Am. Chem. Soc.*, **63**, 1073 (1941).(3) J. Thiec and J. Wiemann, *Bull. Soc. Chim. France*, 207 (1958).

tum yields were almost independent of inert gas pressures, but approximately 1 atm. of inert gas did lower $\Phi_{C_2H_2}$ and $\Phi_{C_5H_6}$ to a significant extent. In the limiting case of high pressure, which is best achieved in solution, $\Phi_{C_2H_2}$ and $\Phi_{C_5H_6}$ were lowered by a factor of 4. At the same time $\Phi_{CH_3C_6H_5}$ did not change within experimental uncertainty. The quantum yields were independent of temperature and incident intensity (factor of 3 in I_0). Addition of 2–36 mm. of oxygen to BCHD at 10 mm. during photolysis did not change the quantum yield of any of the products within experimental error.

Since oxygen did not affect the quantum yield, it appears reasonable to assume that none of the products originate from the triplet state.⁴ The 2537-Å. radiation most probably excites a molecule to the upper vibrational level of the first excited state from which it decomposes immediately before it has a chance to be deactivated by collision. Since $\Phi_{C_2H_2}$ and $\Phi_{C_5H_6}$ were lowered by a factor of 4 in the liquid phase and since quadricyclene is not a product in the gas phase photolysis (confirmed by n.m.r. analysis), then its formation in the liquid phase photolysis, where deactivation is much more effective, suggests that it arises from lower vibrational levels. It is to be noted that $\Phi_{CH_3C_6H_5}$ is almost a factor of 10 lower than $\Phi_{C_2H_2}$ or $\Phi_{C_5H_6}$ which seems to indicate that it may come either from a different vibrational level of the first excited state or from a different electronic state altogether. The mechanism of toluene formation may be visualized as follows.



Mesomeric biradicals of the above type are known in terpene chemistry.^{5,6} Preliminary experiments showed some trend to decreased quantum yields at pressures below 4 mm.; a study of this effect is under way.

Acknowledgment.—The author wishes to express his sincere thanks to Drs. K. O. Kutschke and R. A. Back for many suggestions and encouragement during the progress of this work.

(4) V. Brunet and W. A. Noyes, Jr., *ibid.*, 121 (1958).(5) H. Pines and J. Ryer, *J. Am. Chem. Soc.*, **77**, 4370 (1955).(6) R. L. Burwell, Jr., *ibid.*, **73**, 4461 (1951).

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RECEIVED OCTOBER 7, 1963

A 100-Mc. Nuclear Magnetic Resonance and Nuclear Magnetic Double Resonance Study of Puromycin

Sir:

In a recent paper by Jardetzky¹ a conformational structure was proposed for puromycin on the basis of 60-Mc. n.m.r. data. Our examination of the same compound at 100 Mc. using a Varian HR-100 spectrometer equipped to accomplish proton-proton spin decoupling² (n.m.d.r.) has allowed us to assign the various proton

(1) O. Jardetzky, *J. Am. Chem. Soc.*, **85**, 1823 (1963).(2) L. F. Johnson, *Varian Tech. Info. Bul.*, Vol. 3, No. 3 (1963), and references therein.

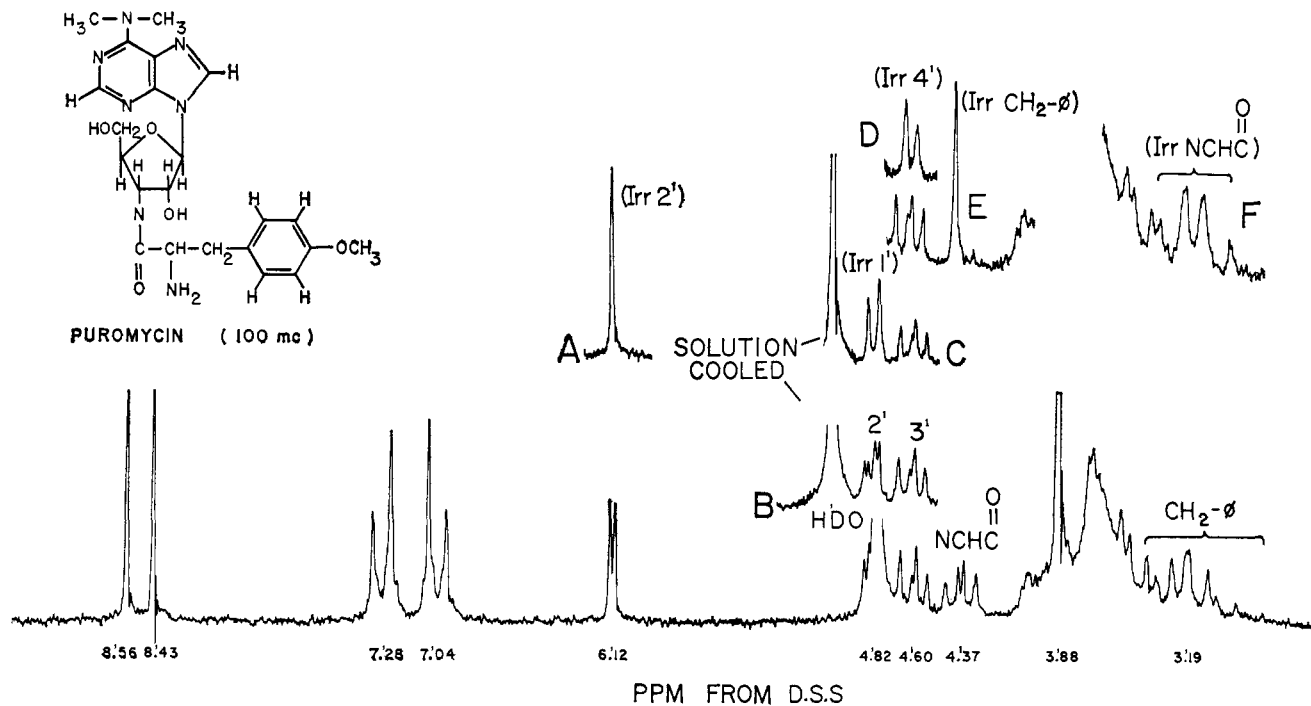


Figure 1.

signals in a different manner. Our interpretation of these new data does not require a folded conformation having the benzene ring over the $C_5'H_2$ group.

Figure 1 shows the 100-Mc. spectrum, including spin-decoupling data, of a 45-mg. sample of puromycin dihydrochloride³ dissolved in 0.5 ml. of D_2O . Chemical shifts are measured relative to the methyl peak of 1.5 mg. of 2,2-dimethyl-2-silapentanesulfonic acid sodium salt^{4,5} (DSS) added as an internal reference.

As in the earlier paper, the $C_1'-H$ is assigned to the 2.5-c.p.s. doublet seen 6.12 p.p.m. from DSS. This doublet could be made to collapse to a singlet by simultaneously irradiating with a relatively large side-band component of the radiofrequency field 129 c.p.s. upfield from the $C_1'-H$ resonance (see Fig. 1, insert A). This confirms the $C_2'-H$ signal as the pair of doublets at 4.82 p.p.m. (see insert B where the otherwise interfering HDO resonance has been shifted toward lower field by cooling the solution slightly). Similarly, the 2.5 c.p.s. splitting in the $C_2'-H$ pattern can be removed by irradiating at the $C_1'-H$ resonant frequency while observing the $C_2'-H$ signals (see insert C). The obvious tilt in the remaining doublet pattern suggests that the spin-coupled $C_3'-H$ chemical shift is nearby. This is verified by removing one of the doublings in the adjacent pattern, 4.60 p.p.m., through another double resonance experiment (see insert D). Thus, inserts C and D show that the patterns at 4.82 and 4.60 p.p.m. have a mutual spin coupling of 5.5 c.p.s., and therefore $C_3'-H$ must be assigned to the pattern at 4.60 p.p.m. The irradiating frequency which produced the pattern of insert D is 58 c.p.s. toward higher field, thus establishing the $C_4'-H$ chemical shift at 4.02 p.p.m. The four-line pattern centered around 4.37 p.p.m. must therefore be due to phenylalanine α -CH proton split twice by spin coupling to the adjacent β - CH_2 group. The average chemical shift of these adjacent CH_2 protons, 3.19 p.p.m., is measured by determining the frequency of the large irradiating field which causes the CH pattern at 4.37 p.p.m. to collapse to a single peak (see

insert E). Likewise, observation of the CH_2 signals, while irradiating the pattern of signals at 4.37 p.p.m., reveals the perturbed pair of doublets shown in insert F. The slight nonequivalence of these CH_2 protons is due to asymmetric substitution on the adjacent carbon atom.

This new assignment of the n.m.r. spectral data of puromycin means that the $C_5'-H_2$ signals must lie between 3.5 and 4.0 p.p.m., a value not unlike that found in other purine ribosides.⁶ In addition, in phenylalanine the average of the CH_2 chemical shifts, 3.19 p.p.m., is in accord with that of other similar benzylic CH_2 groups.⁷

The folded conformation proposed by Jardetzky accounted for an apparently unusual $C_5'H_2$ chemical shift arising from magnetic anisotropy of the benzene ring. Having reassigned the spectrum as discussed above, the folded form is not necessary and in all probability the phenylalanine moiety exists as an ordinary extended chain.

(6) Unpublished data, see also references given in footnote 1.

(7) For example, the average β - CH_2 shift in *p*-hydroxyphenylalanine in D_2O was measured to be 2.98 p.p.m. from DSS.

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RECEIVED AUGUST 19, 1963

The Cleavage of Tyrosyl-Peptide Bonds by Electrolytic Oxidation

Sir:

Efforts to increase selectivity in the nonenzymatic cleavage of tyrosyl-peptide bonds¹ have stimulated an exploration of techniques such as electrolytic oxidation. At a platinum anode, phloretic acid (I) is converted into its dienone lactone (II) in 20% yield.² Under somewhat modified conditions, phloretylglycine (III) is cleaved to II and glycine to an extent of 30–50%.

The electrolysis is effected at 25° with catholyte and anolyte in separate compartments connected by an agar

(1) J. G. Wilson and L. A. Cohen, *J. Am. Chem. Soc.*, **85**, 564 (1963).

(2) A. I. Scott, P. A. Dodson, F. McCapra, and M. B. Meyers, *ibid.*, **85**, 3702 (1963). We are indebted to Prof. Scott for advising us of his findings prior to publication.

(3) Obtained from Nutrition Biochemicals, Cleveland 28, Ohio.

(4) G. V. D. Tiers and R. I. Cook, *J. Org. Chem.*, **26**, 2097 (1961).

(5) Obtained from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York.