

## COMMUNICATIONS TO THE EDITOR

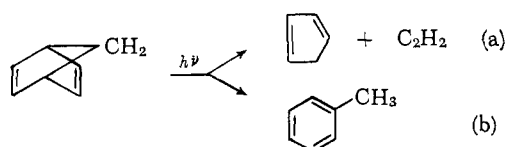
Photolysis of  $\Delta^{2,5}$ -Bicyclo[2.2.1]heptadiene in the Vapor Phase

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.<sup>1</sup> 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 ( $\lambda_{\max}$  2400 Å.,  $\epsilon$  3000)<sup>2</sup>; the infrared spectrum of product cyclopentadiene was found to be identical with that in the literature.<sup>3</sup> 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  $4.21 \times 10^{13}$  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 <sub>2</sub> 300	0.50	0.49	0.048
12.5	H <sub>2</sub> 690	0.45 <sup>b</sup>	0.42 <sup>b</sup>	0.040 <sup>b</sup>
12.0	He 650	0.42 <sup>c</sup>	0.41 <sup>c</sup>	0.050 <sup>c</sup>
12.0	ether sol.	0.12	0.14	0.042

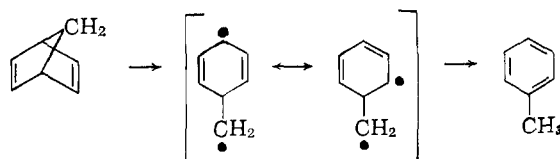
<sup>a</sup> Average of 25 experiments. <sup>b</sup> Average of 5 experiments. <sup>c</sup> Average of 3 experiments.

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.<sup>4</sup> 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.<sup>5,6</sup> 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).

DIVISION OF PURE CHEMISTRY  
NATIONAL RESEARCH COUNCIL  
OTTAWA 2, CANADA

B. C. ROQUETTE

RECEIVED OCTOBER 7, 1963

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

Sir:

In a recent paper by Jardetzky<sup>1</sup> 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 decoupling<sup>2</sup> (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.