

with the cation in a time too short to allow for polymerization in the absence of a solid acting as a stabilizing agent for the conjugate electron.<sup>3c</sup>

The study reported here differs from the above experiments in that (a) the initial species are produced by the irradiation (vacuum ultraviolet) of pure isobutylene, and (b) polymerization is carried out in the presence of an applied electric field. The first part ensures that one is dealing with known initial species produced in the vapor phase by well-studied ion-molecule reactions and the second is designed to eliminate the need for an added gegenion or a heterogeneous surface for the polymerization process.

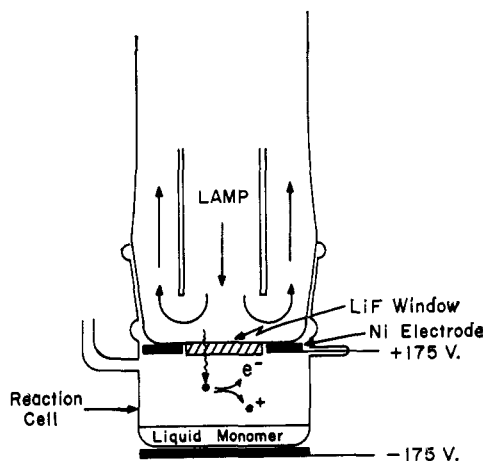
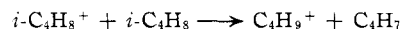


Figure 1.

A modified high intensity resonance light source ( $\sim 10^{18}$  quanta/sec.) emitting the krypton lines (1165 and 1236 Å.) was employed for this process. This energy is sufficient to produce photoionization in isobutylene.<sup>5</sup> The details of the light source were reported previously.<sup>6</sup> Various designs for the placement of the electric field were investigated. One electrode was always near the window of the light source (as shown in Fig. 1), and the other on the bottom of the reaction vessel below some liquefied monomer. The only successful experiments were those in which the cathode is placed on the outside of the reaction vessel, below the liquid monomer (see Fig. 1). Placing the cathode on the inside produced no measurable yield. Similarly, runs with reversed polarity produced no polymer, whereas reversing again to the proper polarity gave an immediate visual formation of polymer. The yield (ca. 0.2 g. in 1 hr.) and molecular weights (ca. 1-4 million) were approximately independent of the applied voltage from 90 to 900 v. A photoionization cell of dimensions similar to the reaction cell and filled with pure gas at the same pressure showed that 90 v. was still on the linear portion of a voltage-current plot, hence indicating that this pressure adequately quenches any multiplication processes. The reaction vessel was stirred and kept carefully at the selected temperature between  $-115$  and  $-145^\circ$  with a low temperature thermostat. For a twofold increase in intensity the yield increased by over a factor of three, whereas the molecular weight showed essentially no change. Increasing

the surface by the addition of glass wool had no effect on yield or molecular weight.

The conclusions from the above would be consistent with an ion-molecule reaction in the liquid phase initiated by *t*-butyl carbonium ions from the gas phase. These carbonium ions are formed by hydrogen abstraction, such as has been observed at higher pressures in the mass spectrometer.<sup>7</sup> The rate of initiation at these



light intensities appears to be controlled by the rate of production of primary ions by the light source. Much higher intensities appear to be required to saturate the electrodes with as many initiating carbonium ions as could be stabilized by the applied field. The external cathode most likely serves to prevent annihilation of the ion at the electrode which would thus lower the concentration of initiating species. The eventual chain length may be determined by precipitation rather than by the time necessary for the polymer to find an electron, in which case the polymer might be "live." Perhaps most important, the absence of surface effects in this polymerization leads one to conclude that this may well be a case of a homogeneous ionic reaction in the liquid phase containing only one component (isobutylene), initiated by irradiation from an external light source. This would then be a method of producing known ions in the gas phase, but studying their reactions in condensed media. The composition of the medium is thus not limited but can be varied at will. Furthermore, the reactions of the ions can be studied in many cases without complicating free-radical side reactions, such as are often present in systems exposed to high energy radiation.

(7) (a) F. W. Lampe, *J. Phys. Chem.*, **63**, 1986 (1959); (b) V. L. Tal'roze and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR*, **86**, 909 (1952).

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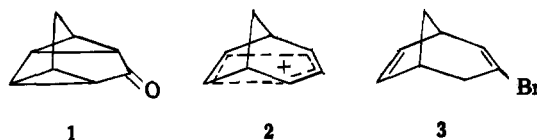
J. J. SPARAPANY

RECEIVED FEBRUARY 21, 1964

### Tetracyclo[3.3.0.0.<sup>4,6</sup>0<sup>2,8</sup>]octan-3-one. A Novel Dicyclopentyl Ketone

Sir:

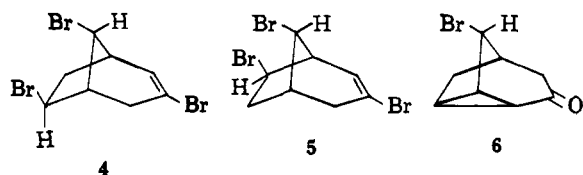
In the course of studies directed toward a synthesis of bicyclo[3.2.1]oct-6-en-3-one, we have discovered a convenient route to the novel tetracyclo[3.3.0.0.<sup>4,6</sup>0<sup>2,8</sup>]octan-3-one (1). This ketone and the derived epimeric alcohols are conceivable precursors to a non-classical cation system such as 2. The present report relates the preparation, structure proof, and properties of 1.



(5) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectr. Radiative Transfer*, **2**, 369 (1962).

(6) E. W. Schlag and F. J. Comes, *J. Opt. Soc. Am.*, **50**, 866 (1960).

The dibromocarbene adduct of norbornadiene was reduced with lithium aluminum hydride to pure 3-bromobicyclo[3.2.1]octa-2,6-diene (**3**).<sup>1</sup> Bromination of **3** in ether at  $-10^{\circ}$  afforded an 84% yield of a crystalline tribromide, m.p.  $100-101^{\circ}$ . *Anal.* Calcd. for  $C_8H_7Br_3$ : C, 27.85; H, 2.60; Br, 69.51. Found: C, 27.62; H, 2.60; Br, 69.39. Several possibilities were available for the structure of the tribromide; however, the spectral data are consistent with either 3,6,8- (**4**) or 3,7,8-tribromobicyclo[3.2.1]oct-2-ene (**5**). Pertinent n.m.r. data are  $\delta$  6.14 (1 H), 2 doublets,  $J_1 \sim 7.4$  c.p.s.,  $J_2 \sim 2.0$  c.p.s. (C-2);  $\delta$  4.45 (1 H), singlet (*syn*-C-8);  $\delta$  4.35 (1 H), triplet,  $J \sim 5.0$  c.p.s. (*endo*-C-6 or C-7); and a complex pattern between  $\delta$  3.16 and 2.26 (6 H).



Hydrolysis of the tribromide in aqueous ethanol containing sulfuric acid at  $50^{\circ}$  led to the bromoketone **6** (56%), m.p.  $56.5-57.8^{\circ}$ . *Anal.* Calcd. for  $C_8H_7OBr$ : C, 47.78; H, 4.51; Br, 39.75. Found: C, 47.81; H, 4.53; Br, 39.47. The n.m.r. spectrum showed a singlet (1 H) at  $\delta$  4.34; complex patterns at  $\delta \sim 1.74$  (2H), 2.05 (2H), and 2.38 (4H). The infrared spectrum showed  $\nu_{\max}^{CHCl_3}$   $1720\text{ cm}^{-1}$ . Structure **6** is best accommodated by these data.

When the bromoketone **6** was treated with potassium *t*-butoxide, an excellent yield of a halogen-free ketone, m.p.  $69.5-70.5^{\circ}$ , was obtained. *Anal.* Calcd. for  $C_8H_8O$ : C, 79.97; H, 6.71. Found: C, 79.76; H, 6.93. The dinitrophenylhydrazone derivative melted at  $225-226^{\circ}$  (dec.). *Anal.* Calcd. for  $C_{14}H_{13}N_4O_4$ : C, 56.00; H, 4.03; N, 18.66. Found: C, 56.06; H, 4.28; N, 18.46. The ketone was assigned the structure **1** on the basis of its spectral properties:  $\nu_{\max}^{CCl_4}$   $1720\text{ cm}^{-1}$ ;  $\lambda_{\max}^{EtOH}$  281, 205  $m\mu$  ( $\epsilon$  50, 5360); n.m.r. complex pattern between  $\delta$  1.3 and 2.6. Unambiguous evidence for structure **1** is given by the mass spectrum<sup>2</sup> (Fig. 1) which confirmed the molecular formula. Of equal significance is the remarkable similarity of the mass spectrum of quadricyclane<sup>3</sup> and other  $C_7H_8$  isomers.<sup>4</sup> Since a primary process of decomposition of **1** upon electron impact would be expected to be the loss of carbon monoxide, this correspondence was not unexpected.

The ketone **1** showed no exchange of deuterium (mass spectrum) when heated with sodium ethoxide and deuterioethanol. Cleavage with sodium amide in dioxane afforded all *cis*-3-carboxamidotricyclo[4.1.0.-0<sup>2,4</sup>]heptane (**7**), with m.p.  $209-210^{\circ}$ ,  $\nu_{\max}$  1680, 1590

$\text{cm}^{-1}$ . *Anal.* Calcd. for  $C_8H_{11}NO$ : C, 70.04; H, 8.04; N, 10.21. Found: C, 70.01; H, 8.24; N, 10.45. Reduction of **1** with sodium borohydride in methanol afforded a mixture of two alcohols (**8** and **9**), m.p.  $82-85^{\circ}$ , in the ratio 80:20 as determined by gas chromatography. Oxidation of the mixture with chromic acid regenerated the starting ketone. On the assumption that the bottom side of **1** is least hindered, the major component of the alcohol mixture is considered to be the *exo* isomer **8**.

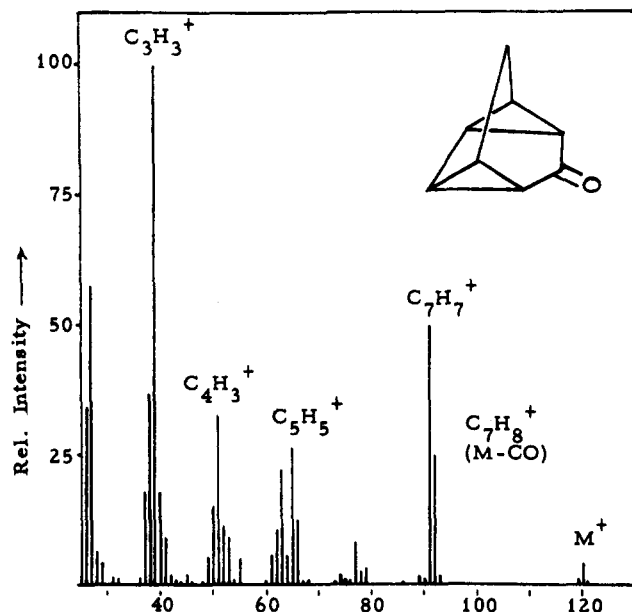
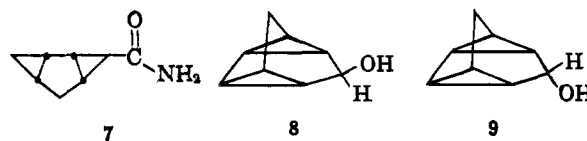


Figure 1.

An n.m.r. spectrum of **1** was taken in concentrated  $H_2SO_4$ , from which solution dilution with water allowed 35% recovery of ketone. A noticeable simplification of the spectrum took place, but conclusions regarding



the significance of the observation must await further data.<sup>5</sup>

**Acknowledgment.**—This work was supported by the Alfred P. Sloan Foundation.

(5) NOTE ADDED IN PROOF.—The homologous tetracyclic ketone, quadricyclanone, has recently been reported: P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 1270 (1964). Compound **1** is also quite polar, and its measured dipole moment in benzene at  $25^{\circ}$  ( $\mu = 3.74$  D.) is unusually large.

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### The Proton Magnetic Resonance Spectra and Rotational Barriers of 4,4'-Disubstituted Biphenyls<sup>1</sup>

Sir:

We present in this communication results of a study of the proton magnetic resonance spectra of 4,4'-

(1) Supported by National Science Foundation Grant G11279. Abstracted in part from a thesis submitted by W. B. Wise in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, Pittsburgh, Pa., Jan., 1964.

(1) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963). We wish to thank Prof. Moore for informing us of these procedures prior to publication.

(2) The spectrum was obtained with a CEC 21-103C mass spectrometer, stainless-steel inlet system operated at  $170^{\circ}$ , ionization potential 70 e.v., ionization current 50  $\mu$ a., temperature of ion source  $250^{\circ}$ . We are indebted to Prof. D. C. DeJongh for the determination and to Prof. K. Biemann for the use of the spectrometer. A preliminary mass spectrum was obtained through the courtesy of Prof. K. L. Rinehart and Dr. T. H. Kinstle, University of Illinois, with an Atlas CH/4 spectrometer.

(3) Z. Dolejssek, V. Hanus, and H. Prinzbach, *Angew. Chem. Intern. Ed. Engl.*, **1**, 598 (1962).

(4) S. Meyerson, *J. Am. Chem. Soc.*, **85**, 3340 (1963).