

Spectra of these Ir(III) complexes were obtained in dimethylformamide (DMF) and in ethyl alcohol solution. Solutions were prepared by dissolving the solid chelates $[\text{Ir}(\text{bipy})_3(\text{ClO}_4)_3]$ was prepared as previously described;⁸ $[\text{Ir}(\text{phen})_3(\text{ClO}_4)_3]$ was prepared in an analogous manner] and also by heating the stoichiometric amounts of the ligand and the metal ion (from iridium chloride) in refluxing ethyl alcohol for 96 hr or in refluxing DMF for 48 hr. Wavelengths of maximum absorption and emission of these Ir(III) chelates did not depend on the method of preparation or on the solvent. Relative luminescence quantum yields for the chelates (in DMF) were about an order of magnitude less than quinine fluorescence in 0.1 *N* H_2SO_4 ; the intensity of $[\text{Ir}(\text{phen})_3]^{3+}$ was approximately twice the intensity of $[\text{Ir}(\text{bipy})_3]^{3+}$.

Acknowledgment. The authors are grateful to the National Science Foundation for financial support (Grant GP-5449).

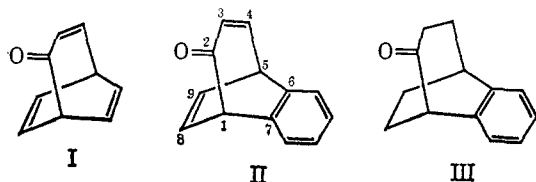
(8) B. Martin and G. M. Waind, *J. Chem. Soc.*, 4284 (1958).

Kenneth R. Wunschel, Jr., William E. Ohnesorge
Department of Chemistry, Lehigh University
Bethlehem, Pennsylvania 18015
Received March 17, 1967

Reaction of Tropone with Benzyne. Formation and Photoisomerization of 6,7-Benzobicyclo[3.2.2]nona-3,6,8-trien-2-one

Sir:

As a vinylog of norbornadiene the bicyclo[3.2.2]nona-2,6,8-triene system and its unknown keto derivative I ("homobarrelenone") have elicited recent synthetic interest.¹ We wish to report the practical one-step synthesis of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (II) by thermal addition of benzyne to tropone, and describe herewith a photochemical rearrangement of this adduct.



The thermal decomposition of a suspension of ~40 mmoles of *o*-benzenediazoniumcarboxylate² in a solution of 38 mmoles of tropone⁵ in anhydrous tetrahydrofuran at 36–37° under nitrogen for 17 hr produced after solvent removal a dark oil. Chromatography over magnesium silicate (benzene-ether) afforded a colorless crystalline adduct in 40% yield,^{6,7} purified by sublimation under reduced pressure (50–60°, 0.10 mm) or recrystallization from hexane, mp 83–84°. Structure II is assigned on the basis of the following data: mass

(1) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Letters*, 4413 (1965).

(2) The benzyne intermediate was generated *in situ* according to the Friedman³ modification of the Stiles⁴ procedure.

(3) L. Friedman, private communication.

(4) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(5) P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

(6) A second uncharacterized product, isolated from the hexane-benzene eluates, was shown to be a 2:1 benzyne-tropone adduct by mass spectrometry (*m/e* 258).⁷

(7) The chromatographic medium used was Florisil synthetic adsorbent, a product of the Floridin Co.

Table I. Nuclear Magnetic Resonance Data

Positional assignment ^a	Chemical shift, ppm from TMS	Coupling constants, ^b cps
5 (broad triplet)	4.19	$J_{5,4} = 8.4$ $J_{5,9} = 6.2$ $J_{5,8} = 1.5$ $J_{5,3} = 0.7$
1 (doublet of triplets)	4.59	$J_{1,8} = 6.5$ $J_{1,3} = 2.0$ $J_{1,9} = 1.5$
3 (doublet of quartets)	5.17	$J_{3,4} = 11.0$ $J_{3,1} = 2.0$ $J_{3,5} = 0.7$
8 (septet)	6.49	$J_{8,9} = 8.0$ $J_{8,1} = 6.5$ $J_{8,5} = 1.5$
9 (septet)	6.84	$J_{9,8} = 8.0$ $J_{9,5} = 6.2$ $J_{9,1} = 1.5$
4 (doublet of doublets)	7.15	$J_{4,3} = 11.0$ $J_{4,5} = 8.4$
Aromatics (4 H) (complex pattern)	~7.13	

^a The positional assignments for hydrogens 8 and 9 were verified by spin decoupling measurements with hydrogens 1 and 5, respectively. ^b The reported *J* values determined from 100-cps sweepwidth spectra are accurate to ± 0.1 cps.

spectral data: *m/e* 182, 181, 154, 153, 152, 128; $\nu_{\text{max}}^{\text{CCl}_4}$ (cm^{-1}) 3070 (m), 3040 (m), 2970 (m), 1675 (s), 1630 (m), 1480 (m), 1455 (w), 1375 (m), 1320 (w), 1280 (w); $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ ($\text{m}\mu$) 225 (ϵ 5720), 263 (704), 351 (137); $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 210 (18,700), 225 (sh) (5620), 263 (743), 331 (sh) (69), 344 (113), 357 (151), 373 (136), 388 (sh) (64); nmr data (CDCl_3), see Table I.⁸ *Anal.* Calcd for $\text{C}_{13}\text{H}_{10}\text{O}$: C, 85.70; H, 5.53; mol wt, 182. Found: C, 85.69; H, 5.41; mol wt, 188 (osmometric in CHCl_3).

Chemical evidence for structure II was provided by its rapid uptake of 2 molar equiv of hydrogen in ethanol with palladium on carbon as catalyst to afford the tetrahydro derivative III as a colorless oil:⁹ mass spectral data: *m/e* 186, 142, 130, 129, 128; $\nu_{\text{max}}^{\text{CCl}_4}$ (cm^{-1}) 3070 (w), 3025 (w), 2930 (s), 2870 (m), 1710 (s), 1490 (m), 1465 (m), 1430 (w); $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ ($\text{m}\mu$) 264 (ϵ 465), 271 (443), 292 (308); $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 259 (sh) (378), 264 (454), 272 (425), 282 (174), 292 (192), 301 (198), 311 (160), 322 (75); nmr (CCl_4) (ppm): 1.94 (6 H, multiplet), 2.14 (2 H, multiplet, $-\text{CH}_2\text{C}(=\text{O})-$), 3.23 (1 H, broad multiplet, position 5), 3.47 (1 H, multiplet, position 1), 7.13 (4 H, singlet, aromatics). *Anal.* Calcd for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.83; H, 7.57. Found: C, 84.06; H, 7.58.

The 1,4 addition of benzyne to tropone is consistent with the reported reaction of maleic anhydride and *N*-phenylmaleimide with tropone.¹⁰ On the other hand, reaction of dimethyl acetylenedicarboxylate reportedly proceeds through the bicyclo[4.1.0]heptadienone valence tautomer.¹¹

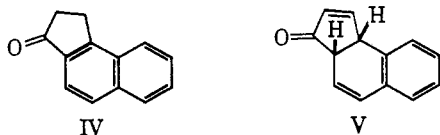
(8) The nmr spectra were recorded with a Varian A-60-A spectrometer equipped with a Model V-6058A spin decoupler. Mass spectral data were recorded on a Hitachi RMU-6D spectrometer. The infrared and ultraviolet data were taken on a Perkin-Elmer Model 337 grating spectrophotometer and a Cary Model 14 spectrophotometer, respectively. The A-60-A and RMU-6D spectrometers were purchased through a National Science Foundation major equipment grant to Brown University.

(9) Purified by short-path distillation at 130° (1.1 mm).

(10) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Buchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

(11) H. J. Dauben and T. J. Pratt, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 10–14, 1967.

Irradiation of adduct II by a medium-pressure mercury lamp (glass filter, acetonitrile solvent, 20°, nitrogen atmosphere) resulted in the gradual formation of a carbonyl maximum near 1704 cm^{-1} with concomitant decrease in the original carbonyl peak near 1675 cm^{-1} . Silica gel chromatography of the reaction products, followed by sublimation at 80° of the principal chromatographic fraction, gave a new crystalline compound: mp 119–120°; mass spectrum: m/e 182, 153, 126, 76; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1707 cm^{-1} ; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ (m μ) 250 (ϵ 61,800), 274 (8700), 284 (10,200), 296 (6600), 330 (2930), 342 (3250); nmr spectrum: A_2B_2 pattern (4 H) with δ_A 2.85, δ_B 3.32, and an aromatic multiplet (6 H) at δ 7.5–8.2. *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.70; H, 5.53; mol wt, 182. Found: C, 85.99; H, 5.75. Taken with the fact that sodium borohydride reduction of this photoproduct generated the ultraviolet spectrum of a 1,2-dialkylnaphthalene, the above data require the photoisomer to contain a conjugated ketone within a five-membered ring fused to the naphthalene nucleus. Three such ketones are possible; all are known and only isomer IV (lit. mp 120–121°) is compatible with the observed melting point. Moreover, the highly structured ultraviolet spectrum of the photoproduct is superimposable with that depicted for authentic ketone IV,¹² and identity was confirmed by comparison with an authentic sample.



It can be shown spectroscopically that ketone IV is not present in the photolysis solution during irradiation but can be instantly generated therein by addition of base. We propose that the primary step in the photoisomerization is the rearrangement of II to the diolefinic ketone V,¹³ with ultimate isomerization to the aromatic IV taking place during the work-up procedure. Further studies of the ground-state and excited-state chemistry of II and its derivatives are in progress.

(12) R. Huisgen and U. Rietz, *Tetrahedron*, **2**, 274 (1958). We are grateful to Professor Huisgen for providing us with a sample of ketone IV prepared by Friedel–Crafts cyclization of β -(1-naphthyl)propionic acid.

(13) The photoequilibrium between 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one and 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one discussed by G. Büchi and E. M. Burgess (*J. Am. Chem. Soc.*, **82**, 4333 (1960)) may offer formal analogy to this type of isomerization.

Joseph Ciabattoni, James E. Crowley
Metcalf Research Laboratories, Brown University
Providence, Rhode Island 02912

Andrew S. Kende

Organic Chemical Research Section, Lederle Laboratories Division
American Cyanamid Company, Pearl River, New York 10965

Received March 22, 1967

Hofmann Elimination. I. An Example of a *cis*-E2 Mechanism¹

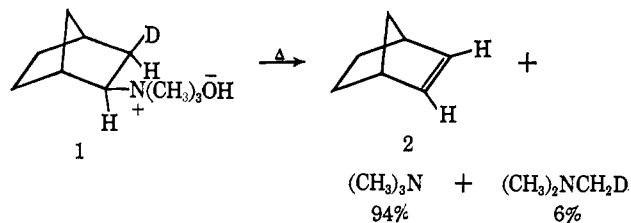
Sir:

Hofmann elimination of quaternary ammonium hydroxides to give olefins has long been thought to

(1) This work was supported in part by a Public Health Service Research Grant, HE 07050, from the National Heart Institute, U. S. Public Health Service.

proceed by a *trans* elimination.² Only two proven exceptions to this have been reported. One of these involves a *cis*-E2 elimination of N,N,N-trimethyl-*trans*-2-phenylcyclohexylammonium hydroxide to give 1-phenylcyclohexene.³ This *cis* elimination presumably takes place because of the activating influence of the phenyl group on the β proton (increased acidity). The other exception involves a predominantly *cis*-ylide elimination of N,N,N-trimethyl-2-*t*-butyl-3,3-dimethylbutylammonium-2-*d*₁ hydroxide to give trimethylamine-*d*₁.⁴

We wish to report an example of a *cis*-E2 elimination mechanism involving a trimethylammonium hydroxide in which there is no activating group other than the trimethylammonium group. It has been shown⁵ that N,N,N-trimethyl-*exo*-2-norbornylammonium hydroxide is smoothly converted to norbornene on heating. We have examined this reaction and find that it proceeds by a *cis*-E2 elimination, as deduced from the following evidence. 2-*exo*-Norbornylamine-3-*exo*-*d*₁ (bp 159–163° (760 mm); n_D^{25} 1.4752; acetamide mp 141.5–142.5°) was prepared from norbornene using diborane-*d*₆ and chloramine⁶ and was then converted consecutively by standard procedures to N,N-dimethyl-2-*exo*-norbornylamine-3-*exo*-*d*₁ (bp 50–52° (6 mm); n_D^{25} 1.4690), N,N,N-trimethyl-2-*exo*-norbornylammonium-3-*exo*-*d*₁ iodide (mp 297–299°), and then to the hydroxide 1. Compound 1 was heated (as the dry solid) at 120° under vacuum until trimethylamine could just be detected in the vapors. This initially produced trimethylamine was analyzed by mass spectrometry⁷ and was found to contain 6% trimethylamine-*d*₁. When the pyrolysis was carried to completion the total trimethylamine was found to contain 17% trimethylamine-*d*₁, with the last traces of vapors containing 21% trimethylamine-*d*₁. This increase in incorporation of deuterium into the trimethylamine after the initial stages of the reaction has been studied by Cope and co-workers⁸ and is due to exchange between the methyl hydrogens of the quaternary hydroxide and the water (containing some deuterium) produced during the reaction. In another experiment the pyrolysis of 1 was carried to completion and the norbornene (2) that was formed was purified and examined by nmr and mass



(2) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(3) G. Ayrey, E. Bunzel, and A. N. Bourns, *Proc. Chem. Soc.*, 458 (1961); A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Am. Chem. Soc.*, **83**, 3859 (1961); S. J. Cristol and F. R. Stermitz, *ibid.*, **82**, 4692 (1960); J. Weinstock and F. G. Bordwell, *ibid.*, **77**, 6706 (1955); R. T. Arnold and P. N. Richardson, *ibid.*, **76**, 3649 (1954).

(4) A. C. Cope and A. S. Mehta, *ibid.*, **85**, 1949 (1963).

(5) A. C. Cope, E. Ciganek, and N. A. LeBel, *ibid.*, **81**, 2799 (1959).

(6) H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *ibid.*, **86**, 3565 (1964); H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 130. The fact that we find total loss of deuterium on Hofmann elimination precludes the possibility of scrambling at the chloramine reaction stage.

(7) For the method used see A. S. Mehta, Ph.D. Thesis, Massachusetts Institute of Technology, 1963.

(8) A. C. Cope, N. A. LeBel, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **83**, 3861 (1961).