

TABLE I
 PYROLYSIS OF TOLUENE AND DEUTERATED TOLUENES AT 750°

Run no.	Carrier gas	Substance	Residence time, sec.	Vol. % toluene	moles $\times 10^4$	Benzene			Methane				
						C_6H_6	C_6H_5D	$C_6H_4D_2$	moles $\times 10^4$	CH_4	CH_3D	CD_3H	CD_4
1	H ₂	C ₆ H ₅ CH ₃	0.7	4.6	4.34	100	7.6	100
2	H ₂	C ₆ H ₅ CH ₃	2	...	8	100	7	100
3	D ₂	C ₆ H ₅ CH ₃	2	...	3	27.5	65.0	6.9	3	53.5	45.2
(Recovered toluene: 87.6% C ₇ H ₈ ; 11.4% C ₆ H ₄ DCH ₃) ^a													
4	H ₂	C ₆ H ₅ CD ₃	0.7	...	6.84	95+	9.0	95+	...
5	D ₂	C ₆ H ₅ CD ₃	2	...	4	27.8	63.2	8.2	4
(Recovered toluene: C ₇ H ₈ D ₂ = 83.8%; C ₇ H ₈ D ₂ = 6.8%; C ₇ H ₄ D ₄ = 9.0%) ^a													

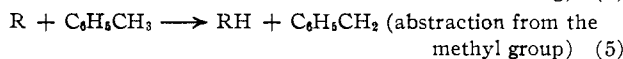
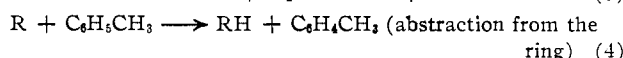
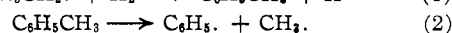
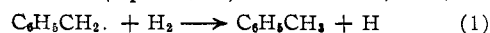
^a The infrared spectrum of these deuterated toluenes was consistent with ring deuteration (J. Turkevich, H. A. McKenzie, L. Friedman and R. Spurr, *J. Am. Chem. Soc.*, **71**, 4045 (1949)) and deuteration in the methyl group.

because bibenzyl, the principal product of the pyrolysis, is not a principal product under the other conditions. In the course of a re-investigation of toluene pyrolysis, using deuterated toluenes and other techniques employed in the radiation chemistry studies, we have observed that the use of hydrogen as a carrier gas produced a remarkable simplification in the results of the pyrolysis.

In our system (described below) pyrolysis of toluene alone or with a helium carrier gas at 750° produced a complex mixture of liquid products, considerable blackening of the quartz tube furnace, and only very small amounts of methane and benzene, the two products in which we were most interested. With hydrogen (or deuterium) as the carrier gas the quartz tube remained clean, and the only isolable products of the pyrolysis were benzene and methane in approximately equal amounts (Table I). No bibenzyl was formed. The conditions used most frequently were as follows: temperature of furnace, 750°; flow rate of H₂ or D₂ = 90 ml./min.; residence time of toluene = 0.7–2.0 sec., volume percentage toluene = about 5; sample weight of toluene = 0.22 g. (2.4 $\times 10^{-3}$ mole). The gases leaving the furnace were passed through a trap at 77°K. (to collect benzene and toluene), intermittently through a gas chromatograph with a molecular sieve column (to analyze for methane), a charcoal trap at 77°K. to collect methane, and a rising film flowmeter. The methane, benzene, and toluene fractions were recovered, purified in a preparatory gas chromatograph and analyzed for isotope composition in a mass spectrometer. Conversion of the toluene was about 2%, and the recovery of toluene was quantitative within the precision of the measurement.

The absence of bibenzyl in the reaction products is only understandable if the benzyl radicals resulting from the usual thermal dissociation of toluene can back-react with the hydrogen (eq. 1).⁵ The methane and benzene must then result from another primary process which is ordinarily negligible. Information about the mechanism of formation of the methane and benzene was obtained by using toluene-*d*₃ and D₂ as well as toluene and H₂. The data so obtained (Table I) can be explained by assuming that the other primary process is a split into phenyl and methyl radicals (eq. 2), and that these then abstract from the carrier hydrogen (or deuterium) or from the toluene (eq. 3, 4, and 5). The isotopic compositions of the benzene and methane then reflect the relative rates of reaction of these radicals with the carrier gas and with

the toluene, and the positions of attack on the toluene molecule.⁶ In Run 3, 65% of the phenyl radicals reacted with deuterium (eq. 3), and about 27.5% reacted with toluene (eq. 4 + 5). In Run 3, also, 45%



of the methyl radicals reacted with deuterium, and 54% reacted with toluene. Since no C₆H₅D was formed in Run 4, phenyl radicals apparently did not abstract from the methyl group of toluene but only from the ring; support for this conclusion is found in the identical magnitudes of the C₆H₅D and C₆H₆ yields when either toluene or toluene-*d*₃ was pyrolyzed with D₂ (Runs 3 and 5). The absence of CD₄ in the pyrolysis products of C₆H₅CD₃ + H₂ (Run 4) shows that the methyl radicals abstract only from the ring also, and not from the methyl group at all.

We wish to stress not only the interest of these preliminary results, but also the novelty of the technique and the simplicity of the results. The only other examples of hydrogen used as a carrier gas for toluene pyrolysis are some early qualitative experiments,⁷ and only a few examples^{4b} of the use of deuterated toluenes to study the pyrolysis of toluene.

Acknowledgment.—We wish to acknowledge helpful conversations about this work with R. B. Ingalls, M. Cher, and Professor M. Szwarc of The School of Forestry, Syracuse, N. Y.

(6) Other processes are certainly going on simultaneously. The deuteration of the recovered toluene in Runs 3 and 5 probably is due to a chain reaction initiated by a D atom adding to the ring followed by thermal ejection of an H atom. One might think that if this D atom added to the ring carbon adjacent to the methyl group, the result might be formation of benzene-*d* and methyl radical, but this cannot be the exclusive process for benzene formation, because the result of it for C₆H₅CD₃ + D₂ mixtures would be exclusively C₆H₅D, but the actual result (Run 5) is formation of considerable C₆H₆. Price^{4a} considers this reaction to be unimportant.

(7) C. D. Hurd "The Pyrolysis of Carbon Compounds" ACS Monograph No. 50. The Chemical Catalog Co., New York, N. Y., 1929 p. 105.

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RECEIVED NOVEMBER 30, 1962

NON-CLASSICAL CARBONIUM IONS: THE STRUCTURE OF STABLE ARYL SUBSTITUTED NORBORNYL CATIONS¹ Sir:

By their distinctive differences in behavior, two classes of carbonium ions may be recognized. "Clas-

(1) Preliminary accounts of this work were presented at National Meetings of the American Chemical Society: 141st, Washington, D. C., March, 1962, Abstracts, p. 28-O, and 142nd, Atlantic City, N. J., Sept., 1962, Abstracts, p. 56-Q.

(3) A. Streitwieser and H. R. Ward, *J. Am. Chem. Soc.*, **84**, 1065 (1962).

(4) (a) S. J. Price, *Can. J. Chem.*, **40**, 1310 (1962); (b) M. Takahashi, *Bull. Chem. Soc. Japan*, **33**, 801 (1960); and (c) the extensive and classic work of Szwarc which was summarized recently in A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth, London, 1955, p. 107.

(5) If the benzyl radical concentration in the pyrolysis zone is 10⁻⁴ that of the toluene, and the usual values for A factors and E values are taken, it can be estimated that the rate of reaction 1 is about 1000 times the rate of the dissociation of toluene into benzyl radicals.

TABLE I
ULTRAVIOLET SPECTRAL MAXIMA OF ARYL SUBSTITUTED
NORBORNYL CATIONS^a

Diaryl ion precursor	Initial λ_{\max} , $m\mu$	Monoaryl analog	λ_{\max} , $m\mu$
Ia	340	Ig	337
Ib	349	Ih	350
Ic	349	Ih	350
Id	353	Ih	350
Ie	381	Ii	381
If	381	Ii	381

^a In concentrated H_2SO_4 . The monoaryl ions were chemically stable under these conditions,^{6b} but the diaryl ions reacted and the ultraviolet maxima shifted with time.

TABLE II
N.M.R. SPECTRUM OF ION FROM If IN CF_3COOH SOLUTION

Position, τ	Multiplicity	Area	Assignment
2.28	Doublet ($1/2$ AB)	4	Aryl H, <i>meta</i> to OCH_3
2.83	Doublet ($1/2$ AB)	4	Aryl H, <i>ortho</i> to OCH_3
5.89	Sharp singlet	6	OCH_3 groups
6.75	Broad singlet	1	Bridgehead H
7.00	Broad singlet	4	CH_2 's α to C+
7.4	Broad singlet	2	Remaining two CH_2 's
8.0	Broad singlet	2	

TABLE III
APPROXIMATE HALF-TIMES FOR AROMATIC MONOSUBSTITUTION

Starting compound	Bromination ^a	Sulfonation (concd. H_2SO_4)	Sulfonation (84.3% H_2SO_4)
If	<1 minute	<1 minute	60 minutes
2- <i>p</i> -Anisylnorbornene	None detected ^b	>3000 hours	>3000 hours
Tri- <i>p</i> -anisylcarbinol	3 hours	2 hours	>3000 hours
<i>p</i> - <i>t</i> -Butylanisole	<1 minute
<i>p</i> -Methylanisole	...	<1 minute	30 minutes
<i>p</i> -Anisylmethylamine	<1 minute	<1 minute	30 hours

^a A saturated solution of bromine in a 4.5 *M* solution of H_2SO_4 in CF_3COOH was added to an equal volume of a solution of aromatic compounds (about 0.25 *M*) in the same solvent. ^b A side reaction of bromination on the bicyclic ring but not the aromatic ring with a half time of about 40 minutes limited the observation time.

sical" carbonium ions are formed from suitable precursors at normal rates predictable by electronic and structural considerations; such "simple" carbonium ions exhibit little stereospecificity in either their formation or in their reaction.² "Non-classical" carbonium ions, provided their precursors have the proper geometry, are generally formed with enhanced rates and their reactions are highly stereospecific. Despite many investigations, the structures of non-classical carbonium ions remain in doubt³; alternative possibilities include single mesomeric "bridged" structures or rapidly equilibrating simple ion mixtures.³ We report here the preparation and structure proof of a stable, "non-classical" carbonium ion.

The unusual properties of carbonium ions in the bicyclo[2.2.1]heptane series have been widely interpreted to support a bridged structure.^{2,4} Although a number of stable substituted monoarylnorbornyl cations have been studied,^{5,6} the structure of such carbonium ions—bridged or simple—remains unproved because of the difficulty of obtaining unambiguous

(2) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; *Chem. Revs.*, **56**, 571 (1956).

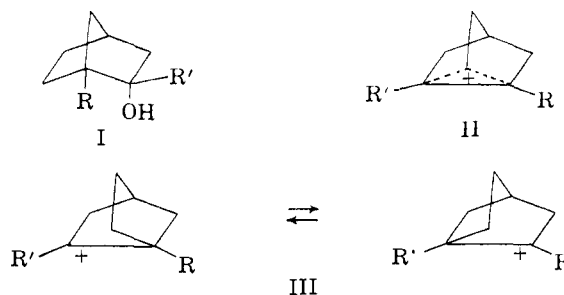
(3) See H. C. Brown in "The Transition State," Special Publication No. 16, Chem. Soc., London, 1962; P. S. Skell and R. J. Maxwell, *J. Am. Chem. Soc.*, **84**, 3963 (1962).

(4) J. A. Berson in P. de Mayo, Ed., "Molecular Rearrangements," Interscience Publishers, Inc., New York, N. Y., in press.

(5) P. D. Bartlett, E. R. Webster, C. E. Dills and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959); P. D. Bartlett, C. E. Dills and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **82**, 5414 (1960).

(6) (a) N. C. Deno, P. T. Groves, J. J. Jaruzelski and M. M. Lugasch, *ibid.*, **82**, 4719 (1960); (b) N. C. Deno, P. von R. Schleyer and D. C. Kleinfelter, *Tetrahedron Letters*, No. 12, 414 (1961); (c) N. C. Deno, unpublished observations, privately communicated; (d) H. G. Richey, Jr., unpublished observations.

structural information. We believe that the symmetry properties of diarylnorbornyl carbonium ions (derived from 1,2-diarylnorbornanols, I⁷) make definitive determination of their structure possible.



For structures I, II and III

- a, $R = R' = C_6H_5$
 b, $R = C_6H_5$, $R' = p-CH_3C_6H_4$
 c, $R = p-CH_3C_6H_4$, $R' = C_6H_5$
 d, $R = R' = p-CH_3C_6H_4$
 e, $R = p-CH_3C_6H_4$, $R' = p-CH_3OC_6H_4$
 f, $R = R' = p-CH_3OC_6H_4$
 g, $R = H$, $R' = C_6H_5$
 h, $R = H$, $R' = p-CH_3C_6H_4$
 i, $R = H$, $R' = p-CH_3OC_6H_4$

Ultraviolet Spectral Behavior.—Because of extended conjugation, diarylnorbornyl cations with bridged structure II should have ultraviolet spectra substantially different from those of analogous monoarylnorbornyl cations (II, $R = H$, $R' = Ar$). If the ions are rapidly equilibrating but asymmetric (III), corresponding monoaryl and diaryl cations should have the same ultraviolet chromophoric groups. The results (Table I) are in accord with the second but not the first prediction and favor asymmetric ion structures (III) for diaryl substituted norbornyl carbonium ions.

Thermodynamic Stability Measurements.—Barring steric influences, the nature and extent of which are hard to predict in this series, the dianisyl cation (from If) would be expected to be *more stable* thermodynamically than the monoanisyl cation (from Ii) if the structures of the ions are symmetrical (II), *less stable* (because of inductive effects of the non-conjugated aryl group) if the structures are asymmetrical (III). For the determination of thermodynamic stabilities of carbonium ions, the percentage of sulfuric acid in water at which the ion is half formed is a convenient measure; the more dilute the acid the more stable the ion.^{6a} The evidence—ion from If half formed in 51% sulfuric acid, ion from Ii half formed in 41% sulfuric acid—favors asymmetrical ion structures (III).

Nuclear Magnetic Resonance Studies.—The n.m.r. spectrum of the dianisylnorbornyl ion (from If) indicated equivalence of both aryl rings (anisyl quartet and methoxyl singlet) and symmetry in the remainder of the molecule (Table II). Either symmetrical

(7) D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

structure II_f or rapidly equilibrating asymmetrical structures III_f are compatible with this result. The effect of cooling gave dramatic evidence in favor of rapidly equilibrating asymmetrical ion structures III_f. The aryl proton peaks lost detail and collapsed into a single broad peak indicating impending non-equivalence of the aryl rings at the lowest temperature it was possible to achieve (-70° in CH_2Cl_2). The corresponding aryl peaks of a model ion (from *p*-anisylcamphenilol)⁵ under the same conditions did not alter significantly.

Chemical Behavior.—Under conditions of complete ionization, symmetrical ion II_f should not undergo rapid aromatic substitution because of the delocalization of positive charge into both aryl rings. Ions III_f would have at any instant only one aryl ring conjugated with the charge; hence, substitution in the non-conjugated ring should be rapid. This latter prediction agrees with the results of semiquantitative experiments, comparing the rates of aromatic substitution of ions from II_f with the behavior of model compounds, by observing the changes in n.m.r. spectra (Table III).

We conclude on the basis of all four experimental criteria that diarylnorbornyl carbonium ions possess rapidly equilibrating asymmetric ion structures III. This result does not rule out the possibility of bridged structures for non-aryl substituted norbornyl or other non-classical carbonium ions, but it stresses the desirability of reopening the question of the structure of such intermediates.³

Acknowledgments.—This work was supported, in part, by a grant from the National Science Foundation (to P. R. S.). We wish to thank Professor Norman C. Deno for his interest, for providing stimulating ideas and discussion, and for experimental assistance.

(8) Alfred P. Sloan Research Fellow.

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RECEIVED OCTOBER 24, 1962

THE MOLECULAR AND CRYSTAL STRUCTURES OF π -CYCLOPENTADIENYL π -CYCLOHEPTATRIENYL VANADIUM

Sir:

The compound $(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)\text{V}$ was prepared by King and Stone,¹ who proved the compositions and showed that the compound was paramagnetic with one unpaired electron per molecule. They named the compound π -cyclopentadienyl π -cycloheptatrienyl vanadium, proposing a structure with the vanadium atom "sandwiched" between five- and seven-membered rings.

Structures of π -cycloheptatrienyl metal complexes have not previously been reported, and reservations as to their existence have been raised.² We report here complete confirmation of the sandwich structure for $(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)\text{V}$, and the first structural information on a π -cycloheptatrienyl compound.

Crystals of the compound are orthorhombic with space group Pnma; lattice constants $a = 11.058 \pm 0.014 \text{ \AA}$, $b = 10.845 \pm 0.016 \text{ \AA}$, $c = 7.929 \pm 0.007 \text{ \AA}$, determined from back reflection Weissenberg diffraction patterns, require four molecules per unit cell.

Intensity data were collected on a General Electric single crystal orienter using a theta-two theta scan

(1) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 5263 (1959).

(2) H. P. Fritz and R. Schneider, *Ber.*, **93**, 1171 (1960).

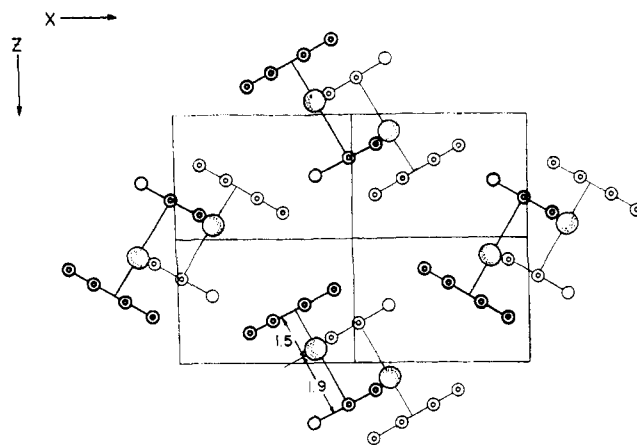


Fig. 1.—Projection onto (010). Heavy lines are molecules at $y = 3/4$, light lines are molecules at $y = 1/4$.

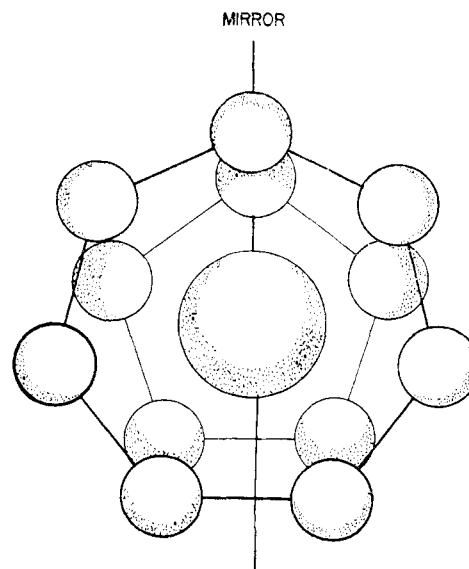


Fig. 2.—Projection of molecule perpendicular to the molecular axes.

technique. A three dimensional Patterson map led to vanadium atom coordinates $x/a = 0.144$, $y/b = 0.25$, $z/c = 0.464$ in $4c$ of Pnma, so that the molecules possess mirror symmetry. A complete but not thoroughly refined structure has been found.

The vanadium atom lies between C_5 and C_7 rings (Fig. 1 and 2); the rings are bisected by mirror planes so that one apex carbon atom of each ring lies on a mirror plane as shown in Fig. 2.

The perpendicular distance from the vanadium atom to the C_7 ring is 1.50 \AA , while the distance to the C_5 ring is 1.90 \AA . The V-C (7-ring) distances are 2.25 \AA , while the V-C (5-ring) distances are 2.23 \AA , equal within the limits of our current stage of refinement. It appears, then, that V-C distances are the main factor controlling the distance of vanadium to the two rings. The C-C distances are 1.403 \AA in the C_7 ring and 1.424 \AA in the C_5 ring. Both rings are symmetrical within our present accuracy. The bonding here is not to be likened to that in $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$ ³; in cycloheptatriene complexes the presence of a methylene carbon prevents equivalence of the ring carbons.

The present discrepancy factor, R , is 0.186 for 969 observed reflections; for the $\{hk0\}$ data only $R = 9.6\%$.

At this stage of refinement it appears that the torsional amplitudes of the rings about their common axis

(3) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).