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A NOVEL AND CONVENIENT SYNTHESIS OF ARYLNORBORNYL CATIONS

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BICYCLOHEPTADIENE (I) reacts with benzene and its derivatives in 97% sulfuric acid to form ions, the properties of which resemble those of α-monoaryl cations. Furthermore, the ions so formed are identical with those produced by the action of concentrated sulfuric acid upon corresponding 2-aryl (II)[1] and 1-arylnorbornanols (III and IV).[1] Cations from I, II, III, and IV exhibited the same ultraviolet spectra and possessed the same thermodynamic stabilities.

These ions, formulated as VII,[2] are probably formed from II directly, from III and IV by Wagner - Meerwein rearrangement and from I by alkylation to V and/or VI, followed by protonation and 6,2-hydride shift.[3] The cations

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[1] D.C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960. For the synthesis of the arylnorbornanols (II-IV) see D.C. Kleinfelter and P. von R. Schleyer, J.Org.Chem. 26, In press (1961).

[2] N.C. Deno, to be published.

[3] L. Ruzicka in Perspectives in Organic Chemistry (Edited by A. Todd) p. 265. Interscience, New York (1956).

are presumably in equilibrium with hydrocarbons. Like 2-phenylbornyl cations,[4] ion VII (Ar = p-$CH_3OC_6H_5$) gave aryl hydrocarbons on addition of water; 2-p-anisylnorbornene was identified as the major product.

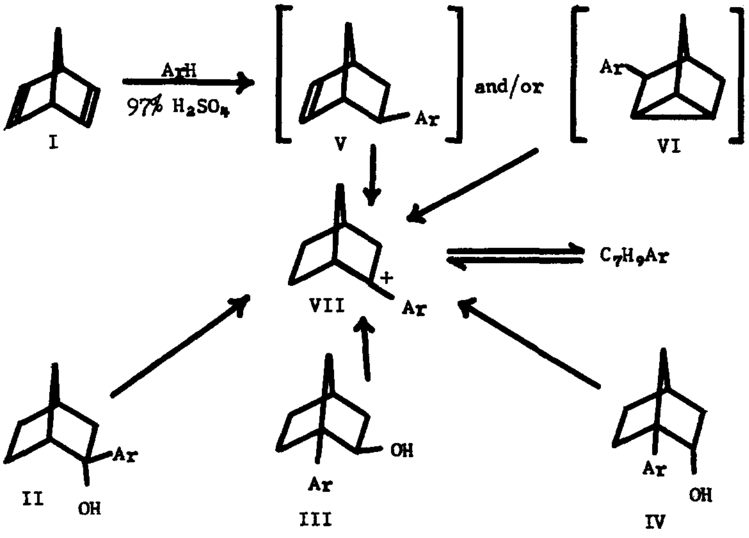

Table 1 summarizes values of λ_{max}, log e, and estimates of the % sulfuric acid at which the concentration of the cation equals concentration of the aryl hydrocarbons. From these latter values, pK_{R^+} constants can be evaluated[4] and plotted against σ^+ substituent constants. The series Ar = C_6H_5, p-ClC_6H_4, p-$CH_3C_6H_4$ and p-$CH_3OC_6H_4$ give ρ about -6, a value similar to that of other aryl cation series.[2,4] These results are pertinent because of recent interest in the structure of monoaryl[1,2,4,5] and diaryl[1] bicyclo-[2,2,1]heptyl carbonium ions.

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[4] N.C. Deno, P. Groves, J. Jaruzelski and M. Lugasch, J.Amer.Chem.Soc. 82, 4719 (1960).

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

TABLE 1. Stability and λ_{max} for 2-Arylbornyl Cations

Ar =	Cation prepared from	λ_{max} (μ)	log e	% H_2SO_4[a]
Phenyl	I,II,III,IV	337	4.58	76
4-Chlorophenyl	I,II,III,IV	365	4.59	77
4-Methylphenyl	I,II,III,IV	360	4.60	66
4-Methoxyphenyl	I,II,III,IV	381	4.69	45 ± 4
		369	4.55	
4-NH_3^+-phenyl	III,IV	327	4.23	92
4-$(CH_3)_2NH^+$-phenyl	II,III,IV	327	3.88	93
3-Methoxyphenyl	III	343	4.26	
2-Methoxyphenyl	II,III,IV	324	4.39	62
2,4-Dimethoxyphenyl	I	460		40 ± 5[b]
2,5-Dimethoxyphenyl	I	464		42[c]
3,4-Dimethoxyphenyl	I	433		40 ± 5[b]
2,4,6-Trimethylphenyl	I	408		72
2,4,6-Trimethoxyphenyl	I	430		40 ± 5[a]
		345		

[a] Acidity required for c_{R^+} = concentration of C_7H_9Ar.

[b] Cloudiness of the solutions in 0-45% H_2SO_4 prevented more precise estimation. These ions can be formed from I in acids as dilute as 75% H_2SO_4.

[c] This ion was unstable in the 42% H_2SC_4 region; this estimate may be in error.