Table I. Acidities and Spectra of α-Ferrocenylcarbonium Ions
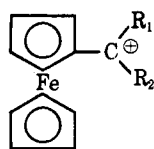
R_1	R_2	λ_{max}, mμ (log ϵ)^a	pK_R
H	H	256 (3.95)	-1.28^b
CH$_3$	H	258 (4.04), ca. 375 (2.62)	-0.66^b
C$_6$H$_5$	H	Ca. 227 (4.03), 252 (4.00), 280 (3.92), 329 (4.08), 405 (3.50)	$+0.4,^b +0.1^c$
C$_6$H$_5$	C$_6$H$_5$	258 (4.06), 365 (4.08), ca. 560 (3.37)	$+0.75^c$

^{a} In 58% H$_2$SO$_4$. ^{b} In aqueous H$_2$SO$_4$. ^{c} In ethanol–water–H$_2$SO$_4$ by comparison with trianisylmethyl cation.

jugation" was put forth.[4]

It seemed desirable to us to investigate the stability of ferrocenylcarbonium ions directly, rather than in the indirect manner allowed by kinetics. Accordingly, we report in Table I preliminary results of a Hammett–Deno type indicator acidity study[5] of several α-ferrocenylcarbonium ions. In all instances, the carbinols are converted in acidic solution to a new species which absorbs in the visible and ultraviolet regions. Reversibility of this conversion was confirmed by recovery experiments, and no further spectral changes were found to occur in more highly acidic solutions up to 96% sulfuric acid. The corresponding carbonium ion is the only reasonable possibility for the absorbing species. Dilute solutions of the carbinol and carbonium ion in acid were stable enough for straightforward spectroscopic studies, except in the case of the diphenylferrocenylcarbonium ion.[6]

The results in Table I demonstrate again the high stability of α-ferrocenylcarbonium ions. But furthermore, a closer examination of these results shows that *the thermodynamic stability of ferrocenylcarbonium ions is several powers of ten greater than kinetics studies indicate.* Several comparisons may be made. (1) Relative solvolysis rates of the acetates of ferrocenylmethanol, α-ferrocenylethanol, phenylferrocenylmethanol, and triphenylmethanol are 0.63:6.6:67:1.00.[3b] From the reported pK_R of triphenylcarbonium ion (-6.63)[5] and presuming twice the sensitivity to structure in ionization as in solvolyses, the ferrocenylcarbonium ions range from 3 to 6 pK units less acidic than predicted. (2) A pK_R value of -17.3 has been reported for 2,4,6-trimethylbenzyl cation.[8] Extrapolation[9] to the ferro-

cenylcarbonium ion using $\sigma^+ - 1.55$ for aryl=ferrocenyl[10] yields a predicted pK_R of -7.4. (3) From published pK_R values of mono- and disubstituted diarylcarbonium ions,[5] a ρ value of -5.2 may be derived. This correlation predicts pK_R for the phenylferrocenylcarbonium ion of -5.4 (vs. the observed value of $+0.1$ to 0.4). A multiple variation treatment of the type of Ritchie[11] raises the predicted value slightly (to ca. -4.0). A similar treatment[11] for the diphenylferrocenylcarbonium ion predicts a pK_R value only about 1.2 units more negative than the observed value.

The results above raise questions concerning the relevance of any kinetic evidence to the question of ferrocenylcarbonium ion structure. Customarily, the stabilities of carbonium ions may be correlated with their rates of formation in solvolysis reactions. The failure of such a correlation in the present instance suggests that the carbonium ion is substantially beyond the transition state along the reaction coordinate, and likely significantly different in geometry as well as energy. The high energy of the transition state (relative to carbonium ion) may reflect a large reorganization of bonding and structure in passing from carbinol to carbonium ion. The present results provide no basis for choice between the "metal participation" and "hyperconjugation" models for the ferrocenylcarbonium ion, since either might involve substantial changes in bonding. However, the remarkable stability of ferrocenylcarbonium ions and the slight additional stabilization achieved by methyl and phenyl substitution both argue for substantial change delocalization, most probably onto the iron. Further speculation does not appear to be warranted at this stage; a more extensive discussion of these results and other work currently in progress in our laboratory will be presented in a full publication.

(4) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967). This paper also gives references to nmr data.

(5) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

(6) The diphenylferrocenylcarbonium ion decomposes to diphenylfulvene.[7] Spectral absorptions were extrapolated back to the time of mixing.

(7) A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, and N. A. Rodionova, *Dokl. Akad. Nauk SSSR*, **160**, 355 (1965).

(8) N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960).

(9) A ρ value for monoarylcarbonium ions may be estimated as -10, as this approximates the total effect of substituents on di- and triarylcarbonium ions (see Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4979 (1958)), and an effective σ^+ value may be estimated for the *ortho*-methyl groups from *t*-cumyl chloride solvolyses (see H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *ibid.*, **79**, 1897 (1957)). The extrapolated value must be considered very rough because of uncertainties in studies of monoarylcarbonium ions.

(10) M. L. Gross, Ph.D. Thesis, University of Minnesota, 1966; based on solvolyses of a series of α-arylethyl acetates.

(11) C. D. Ritchie, W. F. Sager and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 2349 (1962).

(12) National Science Foundation Undergraduate Research Participant, Summer 1967.

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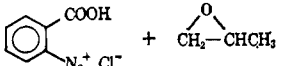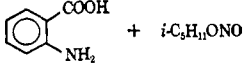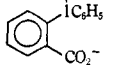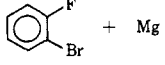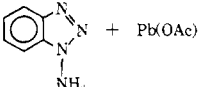## The Identity of Benzyne from Various Precursors

Sir:

Does benzyne generated from various sources exhibit identical properties?[1] We wish to report that for a number of precursors the benzyne formed has identical properties, but that it may *appear* to be different due to the nature of the reactants and reaction conditions. We have also found 1,4-dimethoxyanthracene[2] to be an effective compound to use as a diagnostic tool to test for the equivalency of benzyne under various conditions.

Table I shows that, within the range of experimental error, only one of the benzyne precursors affords an *apparently* different benzyne in that the ratio of center-to end-ring adducts (B/A ratio) is significantly larger for

(1) R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1017 (1963).
(2) A. Etienne and Y. Lepage, *Compt. Rend.*, **240**, 1233 (1955).

Table I. Reaction of 1,4-Dimethoxyanthracene with Benzyne[a]

Benzyne precursor		B-ring/A-ring
(structure with COOH, N₂⁺ Cl⁻) + CH₂—CHCH₃ (with O), $\xrightarrow[70°]{ClCH_2CH_2Cl}$ [b]		2.4
(structure with COOH, NH₂) + i-C₅H₁₁ONO, $\xrightarrow[40°]{CH_2Cl_2}$ [c]		2.6
(structure with I⁺C₆H₅, CO₂⁻), $\xrightarrow[160°]{diglyme}$ [d]		3.5
(structure with F, Br) + Mg, $\xrightarrow[65°]{THF}$ [e]		2.1
(benzothiadiazole structure with S, O, O), $\xrightarrow[10°]{}$ [f]		2.2
(benzotriazole structure with NH₂) + Pb(OAc)₄, $\xrightarrow[25°]{}$ [g]		2.5

[a] Reactions were carried out according to the reported procedures peculiar to each benzyne precursor. Vapor-phase chromatographic analyses were made by using an F&M Model 720 gas chromatograph equipped with SE-30, SE-52, and Apiezon columns. The precision of the results was approximately 10%. [b] F. M. Logullo, Ph.D. Dissertation, Case Institute of Technology, 1965. [c] L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963). [d] E. LeGoff, *ibid.*, **84**, 3786 (1962). [e] G. Wittig and E. Benz, *Angew. Chem.*, **70**, 166 (1958). [f] G. Wittig and R. W. Hoffman, *Chem. Ber.*, **95**, 2718 (1962). [g] Reference 3.

the benzyne reaction using diphenyliodonium-2-carboxylate and 1,4-dimethoxyanthracene. Significantly, benzyne generated by oxidation of 1-aminobenzotriazole[3] has reactivity and selectivity comparable to that of benzyne generated from most other sources, in contrast to the suggestion by Rees and Campbell that benzyne derived from 1-aminobenzotriazole might be different.[4]
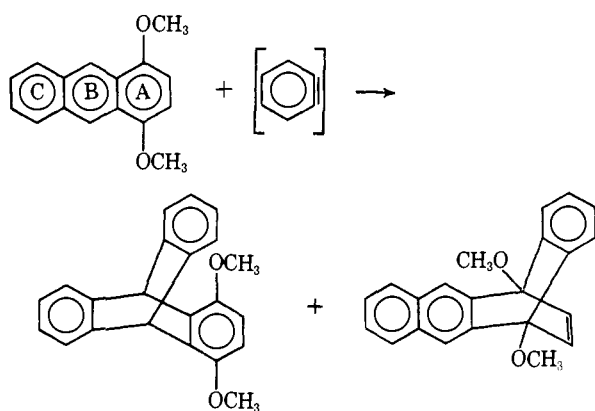
Solvent and temperature changes do not significantly affect the nature of benzyne;[5] in fact, *a priori* the high temperature for the diphenyliodonium-2-carboxylate reaction would lead to a lower B/A ratio rather than a

(3) C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964).
(4) C. D. Campbell and C. W. Rees, *Chem. Commun.*, 192 (1965).
(5) The B-ring/A-ring ratios were not significantly changed over a 40° temperature range nor by the use of acetone, acetonitrile, benzene, 1,2-dichloroethane, diglyme, or tetrahydrofuran as solvents.

higher one, *i.e.*, a higher temperature would give a more reactive and less selective benzyne in contrast to what is observed.

In order to determine why benzyne generated from diphenyliodonium-2-carboxylate appears to be more selective, we compared the relative reactivities of substituted anthracenes for benzyne generated from diphenyliodonium-2-carboxylate and from 2-carboxybenzenediazonium chloride.[6] Table II shows the effects of iodobenzene, which is produced in the decomposition

Table II. Relative Reactivities of Anthracenes with Benzyne[a]

Substituted anthracene	Benzyne precursor[b]	Relative reactivity[c]
9,10-Dimethyl	C	19
9,10-Dimethyl	D	4
9,10-Dimethyl	C[d]	12
9,10-Dimethyl	C[e]	12
9,10-Dimethyl	C[f]	9
9,10-Dimethyl	C[g]	4[h]
9-Phenyl	C	1.0
9-Phenyl	D	0.9
9,10-Diphenyl	C	0.20
9,10-Diphenyl	D	0.24

[a] Vapor-phase chromatographic analyses were carried out as described above. [b] C refers to 2-carboxybenzenediazonium chloride as precursor and D refers to diphenyliodonium-2-carboxylate as precursor, both used as described: ref 7 and F. M. Logullo, Ph.D. Dissertation, Case Institute of Technology, 1965. [c] Relative reactivities were calculated using the expression $\log [(X)/(X_0)]/\log [(Y)/(Y_0)] = k_X/k_Y$, where (X) and (Y) refer to final concentrations of substituted anthracene and anthracene, respectively, and where (X_0) and (Y_0) refer to initial concentrations. [d] One equivalent of iodobenzene added. [e] Ten equivalents of iodobenzene added. [f] One equivalent of iodobenzene added, solvent changed from 1,2-dichloroethane to diglyme, and reaction carried out at 70°. [g] Excess iodobenzene added, solvent changed from 1,2-dichloroethane to diglyme, and reaction carried out at 160°. [h] The meaningfulness of this value is questionable because of the erratic behavior of 2-carboxybenzenediazonium chloride and propylene oxide at 160°.

of diphenyliodonium-2-carboxylate.[7] 9,10-Dimethylanthracene is relatively more reactive than anthracene for a "normal" benzyne (from 2-carboxybenzenediazonium chloride) than for benzyne from diphenyliodonium-2-carboxylate. However, when iodobenzene is added in the 2-carboxybenzenediazonium chloride method, the relative reactivity of 9,10-dimethylanthracene over anthracene is decreased, and when the solvent and temperature conditions are progressively changed to approximate as nearly as possible those for the diphenyliodonium-2-carboxylate method, the observed relative reactivities are comparable to those for the diphenyliodonium-2-carboxylate method. Similar effects are noted for the corresponding study of changes in the B/A ratio of 1,4-dimethoxyanthracene, as is shown in Table III. Therefore, the benzynes produced from the various methods are indeed identical in their reactivity toward the center and end rings of substituted anthracenes. These experiments confirm the value and simplicity of a properly substituted anthracene as a diagnostic tool for benzyne equivalency,[8] and also demonstrate the involvement of reagents peculiar to one method for generating benzyne. Moreover, newer methods of gen-

(6) A detailed account of the relative reactivities of a number of substituted anthracenes will be reported elsewhere.
(7) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962).
(8) B. H. Klanderman, *ibid.*, **87**, 4649 (1965).

Table III. B-Ring/A-Ring Ratios for Reactions of Substituted Anthracenes with Benzyne[a]

Substituted anthracene	Benzyne precursor[b]	B ring/A ring
9,10-Dimethoxy	C	Ca. 28
9,10-Dimethoxy	D	Ca. 14
1,4-Dimethoxy	C	2.4
1,4-Dimethoxy	D	3.5
1,4-Dimethoxy	C[c]	2.6
1,4-Dimethoxy	C[d]	2.6
1,4-Dimethoxy	C[e]	3.2
9-Cyano	C	3.7
9-Cyano	D	3.5
9,10-Diphenyl	C	0.08
9,10-Diphenyl	D	0.09

[a] See footnote a of Table II. [b] See footnote b of Table II. [c] See footnote d of Table II. [d] See footnote f of Table II. [e] See footnote g of Table II.

erating benzyne have now been checked in addition to the limited number examined previously.[1]

The role of iodobenzene most likely involves the formation of weak complexes with the anthracenes, thus causing the anthracenes to become less reactive with the electrophilic benzyne. Moreover, weak complexes are consistent with the small amount of energy required to cause the observed changes. The absence of an effect upon the relative reactivities for 9-phenylanthracene and 9,10-diphenylanthracene (Table II) indicates that complexes may only be formed with the more electron-rich anthracenes. This point is confirmed by the B/A ratios for 9,10-dimethoxy-, 1,4-dimethoxy-, 9,10-diphenyl-, and 9-cyanoanthracenes (Table III). No effect is observed for 9,10-diphenyl- and 9-cyanoanthracene B/A ratios for a change from 2-carboxybenzenediazonium chloride to diphenyliodonium-2-carboxylate as benzyne precursor. However, as noted earlier, for 1,4-dimethoxyanthracene the B/A ratio increases and for 9,10-dimethoxyanthracene the ratio decreases when changing the benzyne precursor in the same manner. These results show that iodobenzene is definitely involved with the anthracenes, and not with benzyne itself as has been observed for silver ion.[9] The idobenzene complexes are most likely weak charge-transfer complexes.

These observations show the pronounced effect that iodobenzene has upon the observed reactivity of benzyne with anthracenes. Thus a new general approach for the control of highly reactive species is available in which changes can be effected by proper conditions of complexing agent, solvent, and temperature.

(9) L. Friedman, J. Am. Chem. Soc., 89, 3071 (1967).

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The Conformation of Nucleosides and Nucleotides. An Application of the Nuclear Overhauser Effect

Sir:

Knowledge of the conformation of nucleosides and nucleotides about the C-1',N-9 bond (the glycosidic bond) has become important to an assessment of the conformation of polynucleotides. Trueblood[1] has considered the question and has established a convention

(1) J. Donohue and K. N. Trueblood, J. Mol. Biol., 2, 363 (1960).

for expressing that conformation in terms of a torsion angle (ϕ_{CN}) that denotes the relative positions of the sugar and the base about the glycosidic bond. The two extreme conformations demonstrated by 1 and 2 in the purine riboside series are designated anti and syn, respectively.

Conformational analysis of the glycosidic bond in the purine riboside series has been difficult in view of the apparently low energy barriers to rotation about that bond.[2] Considerable experimental work has been done using optical rotatory dispersion,[3–6] but no good index of conformation has been found.

Reported in the present communication are nuclear Overhauser effect (NOE) measurements that represent a more direct approach to the conformation problem and that support the view that purine ribosides are conformationally mobile.

The nuclear Overhauser effect[7,8] is observed during nuclear magnetic double resonance experiments and allows the detection of nuclear–nuclear mutual relaxation processes. One observes an enhancement of the absorption intensity of one member of a pair of spatially proximate nuclei as an effect of irradiating the other. Kaiser[9] was the first to report an intermolecular NOE in a protonic system when he studied the mutual interaction of chloroform and cyclohexane, whereas Anet[10] first reported the intramolecular counterpart. Recently, the NOE has been employed in the study of several structural and configurational problems.[11–18]

Examination of molecular models shows that H-8 of the purine nucleosides would be an ideal conformational probe if it were to be observed during a double-resonance experiment of the above type. It is not spin coupled to any other proton, yet its spatial dimensions with respect to other protons in the same molecule allow differentiation among other extreme conformations.[19] For example, in the anti conformation H-8 and H-1' are approximately 3.4 Å apart,[20] whereas in the syn conformation the two atoms are 1.8 Å apart.

(2) A. E. V. Haschemeyer and A. Rich, ibid., 27, 369 (1967).
(3) T. R. Emerson, R. J. Swan, and T. L. V. Ulbricht, Biochem. Biophys. Res. Commun., 22, 505 (1966).
(4) M. Ikehara, M. Kaneko, K. Muneyama, and H. Tanaka, Tetrahedron Letters, 3977 (1967).
(5) W. A. Klee and S. H. Mudd, Biochemistry, 6, 988 (1967).
(6) D. W. Miles, S. J. Hahn, R. K. Robins, M. J. Robins, and H. Eyring, J. Phys. Chem., 72, 1483 (1968).
(7) I. Solomon, Phys. Rev., 99, 559 (1955).
(8) I. Solomon and N. Bloembergen, J. Chem. Phys., 25, 261 (1956).
(9) R. Kaiser, ibid., 39, 2435 (1963).
(10) F. A. L. Anet and A. J. R. Bourn, J. Am. Chem. Soc., 87, 5250 (1965).
(11) M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyama, and K. Nakanishi, Tetrahedron Letters, 321 (1967).
(12) N. Abe, R. Onoda, K. Shiragata, T. Kato, M. C. Woods, Y. Kitahara, K. Ro, and T. Kurihara, ibid., 1993 (1968).
(13) M. C. Woods, I. Miura, A. Ogiso, M. Kurabayashi, and H. Mishima, ibid., 2009 (1968).
(14) M. C. Woods, H.-C. Chiang, Y. Nakadaira, and K. Nakanishi, J. Am. Chem. Soc., 90, 522 (1968).
(15) R. W. Franck and K. Yanagi, J. Org. Chem., 33, 811 (1968).
(16) J. G. Colson, P. T. Lansbury, and F. D. Saeva, J. Am. Chem. Soc., 89, 4987 (1967).
(17) R. H. Martin and J. C. Nouls, Tetrahedron Letters, 2727 (1968).
(18) J. C. Nouls, P. Wollost, J. C. Brackman, and G. van Binst, ibid., 2731 (1968).
(19) Dipole–dipole interactions are distance dependent and T_1 is related to the sixth power of distance in the case of rigid intramolecular interactions and the third power of a size parameter in the case of variable distances (intra- as well as intermolecular). See J. G. Powles, Ber. Bunsenges. Phys. Chem., 67, 328 (1963).
(20) Measured as internuclear distance on Dreiding models using pyramidal N-9.