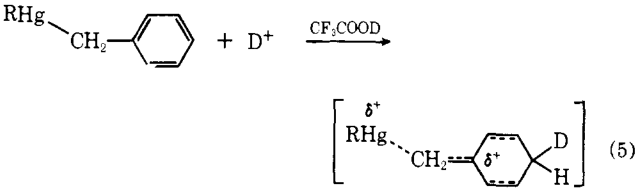
Table I. Rates of Reaction of Organometallic Compounds with $Ph_3C^+BF_4^-$ in Acetonitrile at 29.8° [a]

Compound	k_2, M sec^{-1}	k_2' per hydrogen
Cycloheptatriene	0.413	0.21
Et_4Si	6.8×10^{-7}	5.7×10^{-8}
Et_4Ge	4.8×10^{-5}	4×10^{-6}
Et_4Sn	1.0×10^{-2} (25°)	8.3×10^{-4}
Et_4Pb	5.9	0.49
Et_2Hg	0.9	0.15
$(Me_3SnCH_2)_2CH_2$ [b]	0.115	0.058
$Me_3SnCH_2CH_2Ph$	0.0956	0.048

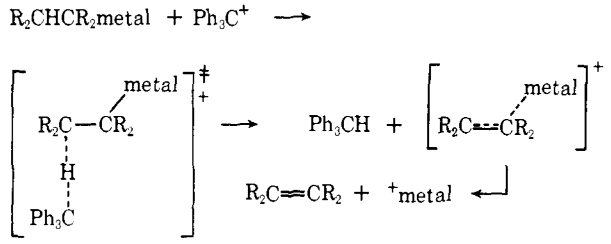
[a] Rates measured spectrophotometrically as pseudo-first-order disappearance of $PhC^+BF_4^-$ except for those of Et_3Si and Et_4Ge which were measured as zero-order rates by glc observation of ethylene. [b] The product of this reaction is allyltrimethyltin identified by nmr spectroscopy.

silicon-substituted carbonium ion. We have strong evidence that reaction 5 is accelerated by vertical



(5)

stabilization[3b] to produce the geometry indicated. These and the observation (Table I) that a second CH_2SnMe_3 accelerates the rate more than does a phenyl group[10] make it very probable that these reactions proceed through the carbonium ion as shown in eq 6.[13-15]



(6)

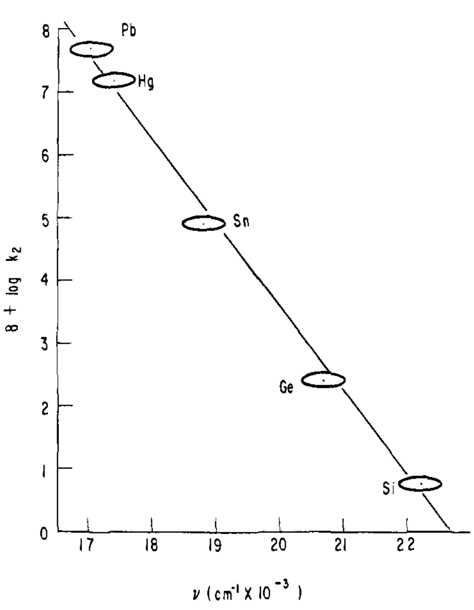


Figure 1. Plot of log k_2' for reaction of Ph_3C^+ with Et_nM (reaction 1) against charge-transfer frequencies of Ph_nMCH_2Ph with tetracyanoethylene.[3b,d] See k_2' per hydrogen in Table I.

A plot of log k_2' against the charge-transfer frequencies of Ph_nMCH_2Ph–tetracyanoethylene (eq 2) in Figure 1 shows that the vertical stabilization by R_nMCH_2– is accurately reflected in the rates of hydride abstraction. This is an additional implication that the principal driving force for hydride abstraction from Et_nM is vertical stabilization of an intermediate carbonium ion by Et_nMCH_2–.[16,18]

This reaction offers an attractive alternative to solvolysis as a way of studying stable cations. We are extending this study to other σ–π conjugated cations.[3b]

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(10) A second neighboring group can accelerate the rate by only a factor of two[11] whereas there is no limit on the acceleration available from a second vertical stabilizing group.[12] Previous results[3d] show that $-CH_2SnMe_3$ inductive effect is like CH_3 so that inductive effects are also excluded.

(11) See C. J. Lancelot and P. v. R. Schleyer (*J. Amer. Chem. Soc.*, **91**, 4296 (1969)) for a discussion of the acceleration provided by two bridging groups.

(12) H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964).

(13) We do not exclude bridging. We only conclude that, in many of the cases we have studied, bridging makes negligible contribution to the stabilization and is therefore of little importance in our discussions of reaction rates or cation stabilizations. Since the energy difference between the symmetrical and unsymmetrical mercurinium ion is thought to be very small, the suggested[14] corner attack in oxymercuration of 7,7-dimethylnorbornene could still partake of the same stabilization of the mercurinium ion as do reactions with the less-hindered norbornene. This interpretation is different from that of Brown and Kawakami[14] who consider the norbornene mercuration intermediate to be like the norbornyl cation obtained by protonation of norbornene.

(14) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(15) The existence of $^+CH_2CH_2SiMe_3$ is clearly demonstrated,[9] and our evidence favors mechanism 6 for other group IV organometallic compounds. However, one-step dehydrometalation is expected for very reactive compounds such as Et_4B^-, etc. Studies of these compounds will be reported later.

(16) O. A. Reutov, E. V. Uglova, V. C. Makhaev, and V. S. Petrosyan, *Zh. Org. Khim.*, 2153 (1970), proposed a cyclic elimination in the reaction of diisobutylmercury with $(C_6H_5)_3CBr$ by analogy to the cyclic mechanism generally written for reduction of Grignard reagents. However, such cis elimination is not favored in reaction 1[17] and it might be incorrect for Grignard reductions. The stereochemistries of these reactions are under investigation.

(17) Unpublished work of M. H. Hall.

(18) The nmr results of Olah and Clifford[7] are consistent with and interpreted in terms of a bridged mercurinium ion. However, our previous evidence[3e] for a mercurinium ion as a reaction intermediate indicated it to be σ–π conjugated and not bridged.[3e] The structure of bridged ions in nonnucleophilic solvents is, in this case, clearly not an accurate description of the transition state leading to the ion. Recent molecular orbital calculations on both $CH_3CH_2CH_2^+$ [19] and $RHgCH_2$-CH^+CH_3[20] seem to confirm our postulate that σ–π conjugation is in general much more important than bridging or fragmentation.

(19) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

(20) R. S. Bach, private communication.

(21) On leave of absence from Institute Ruder Bŏskovic, Zagreb, Yugoslavia.

Joško M. Jerkunica,[21] T. G. Traylor*
Chemistry Department, Revelle College
University of California, San Diego
La Jolla, California 92037

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Single-Crystal X-Ray Structures of Chemotherapeutic Agents. V. The Structures of 5-Diazo-6-methoxy-6-hydrouracil and 2′-Deoxy-5-diazo-6-hydro-O^6,5′-cyclouridine Hemihydrate

Sir:

The 5-diazo derivatives of uracil and uridine have been shown to possess significant carcinostatic activity.[1]

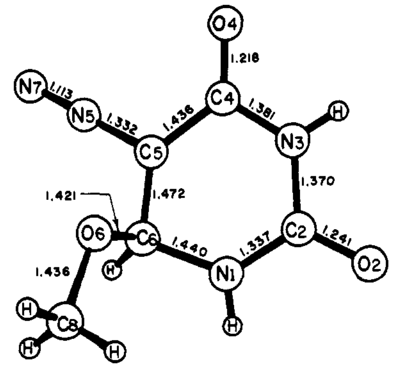


Figure 1. Perspective drawing showing interatomic bond distances in ångströms for 5-diazo-6-methoxy-6(*H*)-uracil (**1**) (esd ≤0.007 Å).

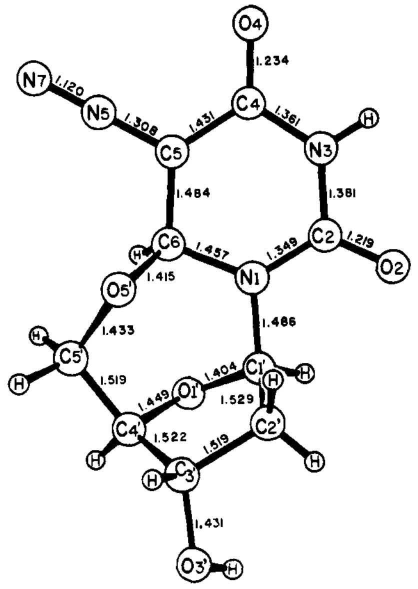
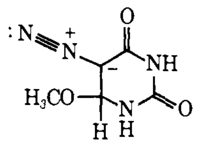
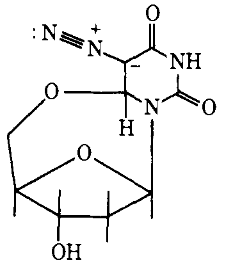


Figure 2. Perspective drawing showing interatomic bond distances in ångströms for 2'-deoxy-5-diazo-6(*H*)-O^6,5'-cyclouridine (**2**) (esd ≤0.007 Å).

However, their structures, particularly the portion associated with the diazo substituent, have never been adequately characterized. In order to provide the structural information necessary for an understanding of the chemical and biological properties of these compounds, we initiated single-crystal X-ray determinations of the two compounds known as 2'-deoxy-5-diazouridine[2] and the "methanol adduct" of 5-diazouracil.[3] These X-ray studies show that the structure previously reported for the diazouridine[2] is incorrect and characterize the structure of the methanol adduct for the first time. Thus, in the methanol adduct, a methoxy group has become covalently bonded to C(6) of the uracil ring to form 5-diazo-6-methoxy-6(*H*)-uracil (**1**), while in the diazouridine, the oxygen of the 5' sugar hydroxyl group is covalently bonded to C(6) of the pyrimidine ring to form 2'-deoxy-5-diazo-6(*H*)-O^6,5'-cyclouridine (**2**). Thus, it becomes apparent that the unsaturated 6 position in this class of compounds is quite electrophilic.



1



2

Although the existence of O^6,5'-cyclonucleosides has been reported,[4] this cyclization had not been postulated for **2**. The structure of the alcohol adducts of 5-diazouracil was essentially unknown, with only one previous, and incorrect, structure having been proposed at an early date.[3b]

Compound **1** ($C_5H_6N_4O_3$) was obtained as thin yellow plates during an attempt to crystallize 5-diazouracil from methanol.[5] The crystals rapidly clouded upon heating above 125° and decomposed at 205–210°. The space group was $P2_1/c$ with unit cell parameters: $a = 10.520$, $b = 6.961$, and $c = 10.297$ Å, $\beta = 105.8°$, density (obsd) = 1.56 (flotation, CCl_4–hexane), and density (calcd) = 1.55 for $Z = 4$. Intensity data were collected on a Picker FACS 1 diffractometer using graphite monochromated Mo Kα radiation. A total of 958 independent reflections was measured of which 659 were observed ($>2\sigma$). The structure was solved by symbolic addition[6] and refined by least-squares methods. The six hydrogen atoms were located in a difference Fourier and the complete structure was refined anisotropically (hydrogen atoms isotropically) to a present agreement residual R of 0.056 for the 659 observed reflections.

Compound **2** ($C_9H_{10}N_4O_5$) crystallizes as yellow rods in space group $P2_12_12$ with four molecules of **2** and two molecules of water per unit cell. The cell parameters were: $a = 27.774$, $b = 7.570$, and $c = 5.148$ Å, density (obsd) = 1.61 (flotation, CCl_4–CH_2I_2), and density (calcd) = 1.62. Intensity data (1038 independent reflections) were collected on the FACS 1 diffractometer using Ni-filtered Cu Kα radiation and the structure was solved using the tangent formula.[7] A molecule of water was found on one of the two independent twofold axes and after initial refinement a difference synthesis revealed the positions of all hydrogen atoms. The entire structure was refined anisotropically (hydrogen atoms isotropically) to a present R of 0.052 for 1031 independent observed reflections.

In addition to establishing the correct chemical structure of **1** and **2**, the X-ray studies afford significant information concerning the bonding of the diazo group in these molecules. Although there have been numerous investigations of the chemistry of aliphatic diazo compounds,[8] this work constitutes the first reported

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(1) (a) J. R. Bateman, E. M. Jacobs, A. A. Marsh, and J. L. Steinfield, *Cancer Chemother. Rep.*, No. **41**, 27 (1964); (b) A. Goldin, H. B. Wood, and R. R. Engle, *ibid.*, 1 (Part 2), 1 (1968).

(2) J. P. Paolini, R. K. Robins, and C. C. Cheng, *Biochim. Biophys. Acta*, **72**, 114 (1963).

(3) (a) F. G. Fischer and E. Fahr, *Justus Liebigs Ann. Chem.*, **651**, 64 (1962); (b) R. Behrend and P. Ernert, *ibid.*, **258**, 347 (1890).

(4) (a) D. Lipkin and J. A. Rabi, *J. Amer. Chem. Soc.*, **93**, 3309 (1971); (b) E. A. Falco, B. A. Otter, and J. J. Fox, *J. Org. Chem.*, **35**, 2326 (1970); (c) P. K. Chang, *ibid.*, **30**, 3913 (1965).

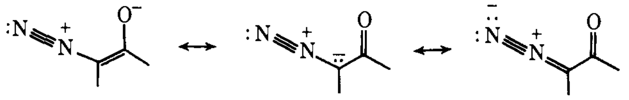
(5) L. B. Townsend and T. C. Thurber, University of Utah, personal communication.

(6) P. Main, M. M. Woolfson, and G. Germain, "LSAM, A System of Computer Programmes for the Automatic Solution of Centrosymmetric Crystal Structures," University of York, York, England.

(7) S. R. Hall, "Direct Phasing Methods Program, UWAC-17," University of Western Australia, revised for the IBM 7090 by H. M. Berman, University of Pittsburgh, 1968.

structural determinations of α-diazocarbonyl compounds by X-ray diffraction.

Compounds **1** and **2** represent a novel type of α-diazocarbonyl compound, for which three main resonance forms can be written: A, B, and C. The interatomic bond lengths shown in the perspective drawings in Figures 1 and 2 indicate that all three forms contribute to the resonance hybrid in **1** and **2**. The C(4)–C(5) bond is intermediate in length between that of a single and a double bond, and is nearly the same as those found in uracil[9] and uridine,[10] while being significantly shorter than that in dihydrouracil (1.515 Å),[11] where no C(4)–C(5) resonance is possible. Similarly, the C(5)–N(5) bond length is intermediate between that of a double and a single bond, and is much shorter than the C–N bond found in aromatic diazonium compounds (1.40 ± 0.02 Å).[12]



A B C

It is of additional interest that the C–N and N–N bond distances reported[13] for diazomethane ($H_2C^-—N^+\equiv N:$) of 1.32 and 1.12 Å agree closely with those found in **1** and **2**, suggesting that these α-diazocarbonyl systems have a carbanion character similar to that of diazomethane. Similar C–N and N–N bond distances of 1.33 and 1.14 Å have also been found in the X-ray structure of 9-diazofluorene.[14]

Acknowledgment. We thank Dr. L. B. Townsend and T. C. Thurber for suggesting this problem and supplying crystals of both **1** and **2**. This work was supported by Contract No. PH-43-67-1186 with the Cancer Chemotherapy National Service Center, National Institutes of Health, and in part by NIH Grant No. GM-01728. We also wish to acknowledge the University of Pittsburgh Computing Center for generous amounts of computing time.

(8) (a) G. W. Cowell and A. Ledwith, *Quart. Rev., Chem. Soc.*, **24**, 119 (1970); (b) Q. P. Studzinskii and I. K. Korobitsyna, *Russ. Chem. Rev.*, **39**, 834 (1970).

(9) R. F. Stewart and L. H. Jensen, *Acta Crystallogr.*, **23**, 1102 (1967).

(10) E. A. Green, University of Pittsburgh, unpublished data.

(11) D. C. Rohrer and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **26**, 546 (1970).

(12) (a) B. Greenbert and Y. Okaya, *ibid., Sect. B*, **25**, 2101 (1969); (b) C. Romming and T. Tjornhom, *Acta Chem. Scand.*, **22**, 2934 (1968); (c) C. Romming, *ibid.*, 17, 1444 (1963).

(13) (a) A. P. Cox, L. F. Thomas, and J. Sheriden, *Nature (London)*, **181**, 1000 (1958); (b) H. Boersch, *Monatsch. Chem.*, **65**, 331 (1935).

(14) P. W. R. Corfield, Ohio State University, personal communication.

D. J. Abraham,* T. G. Cochran, R. D. Rosenstein
Departments of Medicinal Chemistry and Crystallography
University of Pittsburgh, Pittsburgh, Pennsylvania 15213

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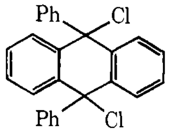
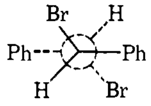
Novel Chemiluminescence Observed on Electroreduction of Aromatic Hydrocarbons in the Presence of Some Alkyl Halides[1]

Sir:

We would like to report a novel and unexpectedly intense chemiluminescent (cl) reaction that results from the electroreduction of solutions containing aromatic hydrocarbons and either 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) or 1,2-dibromo-1,2-diphenylethane (DBDPE) at platinum electrodes. In most previously reported examples of electrochemically generated chemiluminescence (ecl) of aromatic hydrocarbons, the excited state of the hydrocarbon is produced from the annihilation reaction of the radical anion, $R\cdot^-$, of the hydrocarbon with either the radical cation, $R\cdot^+$,[2,3] or another electrogenerated oxidizing agent.[4–6]



$DPACl_2$



meso-DBDPE

It was found that this cl, in a variety of nonaqueous solvents, is about two orders of magnitude greater in luminescence intensity than 9,10-diphenylanthracene annihilation ecl. This indicates that the mechanism by which the excited state is produced during the electrode reaction is different and probably more efficient than $R\cdot^-$ and $R\cdot^+$ annihilation under similar experimental conditions.[7]

All electrochemical and luminescence apparatus, experimental conditions, and solvent purification and organic syntheses procedures were essentially the same as reported previously.[5a,6a,8–11]

Chemiluminescence has previously been observed when $DPACl_2$ is reacted with either the 9,10-diphenylanthracene (DPA) or naphthalene radical anion (produced by sodium metal reduction).[11,12] The light in both cases was identified as DPA fluorescence.[11] The electrochemical reduction of fresh 1 m*M* $DPACl_2$ [0.1 *M* *tert*-butylammonium perchlorate (TBAP)] solutions in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (AN), and tetrahydrofuran (THF) exhibit intense ecl using a platinum electrode.[13]

(1) This research was supported in part by grants from the National Science Foundation, No. GP-9307 and GP-2716.

(2) (a) A. J. Bard, K. S. V. Santhanam, S. A. Cruser and L. R. Faulkner in "Fluorescence," G. G. Gilbault, Ed., Marcel Dekker, New York, N. Y., 1967, pp 627–651; (b) D. M. Hercules in "Physical Methods of Organic Chemistry," 4th ed, Part II, A. Weissberger and B. Rossiter, Ed., Academic Press, New York, N. Y., 1960; (c) A. Zweig, *Advan. Photochem.*, **6**, 425 (1968).

(3) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 209 (1969).

(4) (a) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965); (b) J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, **13**, 1197 (1968).

(5) (a) M. D. Malbin and H. B. Mark, Jr., *J. Phys. Chem.*, **73**, 2992 (1969); (b) D. L. Maricle, A. Zweig, A. H. Maurer, and J. S. Brinen, *Electrochim. Acta*, **13**, 1209 (1968); (c) R. E. Visco and E. A. Chandross, *J. Phys. Chem.*, **72**, 3781 (1968).

(6) (a) M. D. Malbin and H. B. Mark, Jr., *ibid.*, **73**, 2786 (1969); (b) T. Kuwana, *Electroanal. Chem.*, **1**, 228 (1966).

(7) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5968 (1971).

(8) M. E. Peover, *Electroanal. Chem.*, **2**, 1 (1967).

(9) C. K. Mann, *ibid.*, **3**, 57 (1969).

(10) E. Bergmann and O. Blum-Bergmann, *J. Amer. Chem. Soc.*, **59**, 1439 (1937).

(11) E. A. Chandross and F. I. Sonntag, *ibid.*, **88**, 1089 (1966).

(12) M. M. Rauhut, American Cyanamid Co., Stamford, Conn., U. S. Patent 3,391,068 (July 2, (1968)).

(13) It was found that the $DPACl_2$ decomposed at a significant rate at room temperature (fastest in DMF). $DPACl_2$ is known to decompose by several routes.[10,14] Both water (common to all of the above solvents)