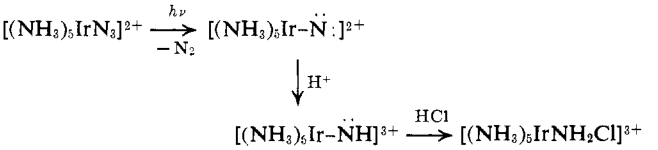
(characteristic of the $[Ir(NH_3)_5NH_2Cl]^{3+}$ ion[4]) reached a maximum optical density corresponding to an 80% yield of the chloramine complex and the band at 279 nm (characteristic of the starting material, $[Ir(NH_3)_5N_3]^{2+}$) disappeared. At this point, the solution was passed through a cation-exchange column (AG50W-X2) which was eluted with about 40 ml of 4 *M* HCl. The eluent was concentrated to dryness by vacuum. The solid residue was then dissolved in a minimum amount of water and concentrated $HClO_4$ was added to precipitate $[Ir(NH_3)_5NH_2Cl](ClO)_3$ in 45% yield. *Anal.* Calcd for $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$: N, 13.40; H, 2.73; NH_2Cl, 8.21; ClO_4^-, 47.57. Found: N, 12.93; H, 2.56; NH_2Cl, 7.75; ClO_4^-, 47.48. The percentage of NH_2Cl was determined by the reaction of the complex with I^- and a determination of the I_2 produced.[4]

The amount of gas liberated by the photochemical reaction was determined using a solution containing 20 mg of $[Ir(NH_3)_5N_3](ClO_4)_2$ dissolved in 2 ml of 0.1 *M* HCl. The solution was degassed by several freeze-thaw cycles, and after irradiation the noncondensable (at liquid nitrogen temperature) gas was collected making use of a Toepler pump. The gas was N_2 with trace amounts of H_2 and O_2, as shown by mass spectrometry. Three experiments gave values of 1.12, 1.15, and 1.10 mol of gas per mole of $[Ir(NH_3)_5N_3](ClO_4)_2$. The 10% excess of gas may result from the photochemical reaction of the product $[Ir(NH_3)_5NH_2Cl]^{3+}$, because under identical conditions irradiation of a solution of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ yielded 0.14 mol of gas per mole of compound. Again the gas was N_2 with traces of H_2 and O_2.

The photolysis of $[Ir(NH_3)_5N_3](ClO_4)_2$ was also repeated in the presence of added iodide ion (2.9×10^{-3} *M* starting material and 1.7×10^{-3} *M* NaI) and of 1 *M* acrylamide. This was done because it had been reported that the presence of iodide ion[1a-c] or acrylamide[1c] quenched the formation of nitrogen for the photochemical reactions of azido metal complexes which proceed through an azide radical. However, the photochemical reaction of $[Ir(NH_3)_5N_3]^{2+}$ liberates exactly 1 mol of N_2 per mole of complex, even in the presence of added iodide ion or acrylamide. In the presence of iodide ion, $[Ir(NH_3)_6]^{3+}$ and I_2 are formed.

The results observed for the photolysis of $[Ir(NH_3)_5N_3]^{2+}$ are consistent with the reaction scheme



$$\begin{tikzcd}[(NH_3)_5IrN_3]^{2+} \arrow[r, "h\nu", "-N_2"'] & {[(NH_3)_5Ir\text{-}\ddot{N}:]^{2+}} \arrow[d, "H^+"] & \\ & {[(NH_3)_5Ir\text{-}\ddot{N}H]^{3+}} \arrow[r, "HCl"] & {[(NH_3)_5IrNH_2Cl]^{3+}}\end{tikzcd}$$

Evidence for the same coordinated nitrene, Ir–NH, intermediate and its reaction with HCl to yield the chloramine product was reported[4] for the thermal reaction of this complex with acid at high concentrations of hydrochloric acid. Clearly, the photochemical decomposition of the azido group in this complex cannot involve the formation of azide radical because the presence of iodide ion or acrylamide does not quench the evolution of nitrogen.

The reaction of $[Rh(NH_3)_5N_3]^{2+}$ with acid does not generate nitrogen,[5] but its photochemical reaction (irradiation at 2537 Å) does evolve nitrogen and also produces the chloramine product $[Rh(NH_3)_5NH_2Cl]^{3+}$. Furthermore, the evolution of nitrogen is not quenched by the addition of iodide ion. These observations suggest that the decomposition of the azide group occurs in the same manner as that outlined above for the corresponding iridium(II) complex.

Irradiated solutions of $[Rh(NH_3)_5N_3]^{2+}$ were monitored at various times for decomposition of the azido complex and formation of $[Rh(NH_3)_5NH_2Cl]^{3+}$. This was done both by measuring the spectra of the resulting solutions and by adding an excess of iodide ion to the solutions and determining the amount of iodine liberated. The results show that the primary photochemical decomposition of the azido complex generates the chloramine in 86% yield; *e.g.*, $\Phi_{NH_2Cl}/\Phi_{dec} = 0.86 \pm 0.02$. However, the rhodium product obtained from the cation-exchange column, as described above for iridium, is a mixture of about 60% $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$ and 40% $[Rh(NH_3)_6]/(ClO_4)_3$. The source of the hexaamminerhodium(III) complex is not known, and it may arise from thermal reactions on the column. The nitrogen content of the isolated material is always high, indicating that photoaquation[6] was not extensive.

Acknowledgment. We thank Dr. Bruce Lane and Mr. Richard Terrell for having done some of the initial experiments on these systems. The research is supported by a grant from the National Science Foundation. The rhodium and iridium were loaned to us by the Matthey Bishop Co.

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[4] B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **94**, 3786 (1972).

[5] C. S. Davis and G. C. Lalor, *J. Chem. Soc. A*, 445 (1970).

[6] T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 1797 (1972).

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Carbene Radical Anions. A New Species of Reactive Intermediate

Sir:

Our interest in the mechanism of reaction of sodium naphthalene with alkyl,[1] vinyl,[2] and aryl[3] halides inevitably led to a consideration of the possible consequences of reaction of this radical anion with polyhalo-organic substrates.[4] Sodium naphthalene (**1**) reacts with alkyl halides *via* dissociative electron transfer to generate an alkyl free radical.[1,5] The free radicals thus produced undergo facile reduction to alkyl anions (or sodium alkyls).[5] One can thus envision two possible mechanistic pathways for the reaction of sodium naphthalene with alkyl geminal dihalides. Initial electron transfer would be expected to generate an α-haloalkyl free radical which could suffer further reduc-

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[1] G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160 (1968); G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, 88, 5363 (1966).

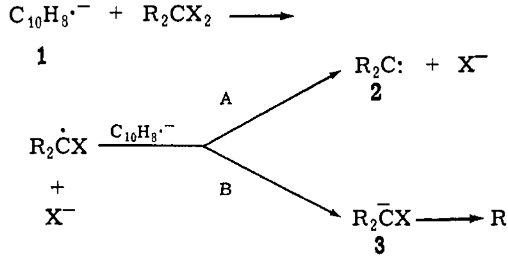
[2] G. D. Sargent and M. W. Browne, *ibid.*, 89, 2788 (1967).

[3] G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).

[4] For a preliminary report of a reaction which follows a different course from those described here, see G. D. Sargent, *J. Amer. Chem. Soc.*, 93, 5268 (1971).

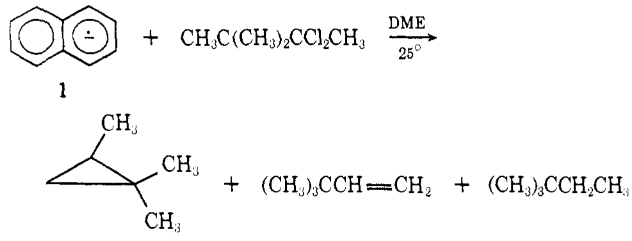
[5] A review: J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971); see also J. F. Garst and F. E. Barton II, *Tetrahedron Lett.*, 587 (1969); J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, 88, 4260 (1966).

tion by either path "A" or path "B." Path "A" involves a second electron transfer to halogen with concomitant carbon–halogen bond fission to generate an alkylcarbene (**2**). Reduction by path B leads to an α-halocarbanion (**3**), a carbenoid which might or might not eliminate halide to yield a free carbene. Carbene species emanating from path B would perforce be singlets, while path A might well produce a mixture of singlet and triplet carbenes.



The possibility that this reaction might provide a simple, convenient method for generating free triplet alkylcarbenes in solution prompted us to initiate a series of experiments designed to test whether typical carbene reactions do result from treatment of alkyl geminal dihalides with sodium naphthalene. We are now pleased not only to report that such reactions are observed, but also to present strong evidence that the carbenes thus produced can be further reduced to carbene radical anions (R_2C^{-}) at a rate competitive with that of intramolecular C–H insertion. To the best of our knowledge the carbene radical anion is a previously undocumented species of reactive intermediate.

tert-Butylmethylcarbene (or its carbenoid counterpart) has been generated in a variety of reactions and yields in all cases predominately 1,1,2-trimethylcyclopropane (**4**) and *tert*-butylethylene (**5**), the products of γ and β carbon–hydrogen insertion, respectively.[6,7] Reaction of 1 *M* sodium naphthalene (**1**) with 1 *M* 2,2-dichloro-3,3-dimethylbutane in 1,2-dimethoxyethane (DME) gave the results indicated below.



4	5	6
19%	38%	11.5%

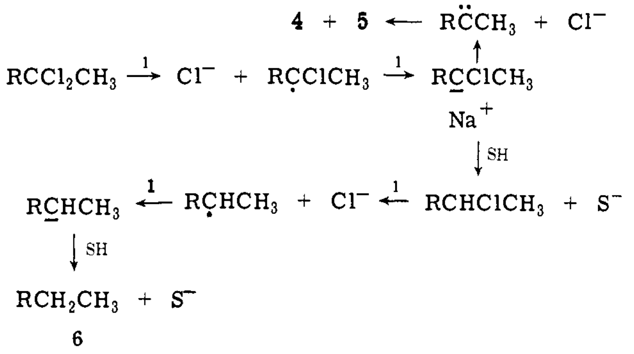
No other halide-derived products more volatile than naphthalene were detected. At least one product is formed in which a six-carbon alkyl fragment is bound to the naphthalene nucleus. This "alkylation" product was expected, and presumably arises from coupling of the naphthalene radical anion with an intermediate alkyl free radical. Although *tert*-butylethylene might derive from a combination of elimination and reduction reactions, the presence of the trimethylcyclopropane in the product mixture is clear evidence that the expected carbene (carbenoid) intermediate is, indeed, generated.

Further evidence that carbenes (carbenoids) do result from reaction of geminal dihalides with sodium naphthalene (**1**) was provided by the observation that 1,1-dichloropropene on treatment with **1** at ambient temperature reacts instantly to give a high yield (*ca.* 70% by glc) of methylacetylene plus at least one other highly volatile hydrocarbon.

Despite providing confirmation of the expected generation of a carbene (carbenoid) intermediate, the results of the reaction of **1** with 2,2-dichloro-3,3-dimethylbutane do raise a serious question: what is the mechanism of formation of 2,2-dimethylbutane?

The most obvious and mechanistically conservative rationale would involve an intermediate α-halosodium alkyl carbenoid sufficiently stable and basic to permit intermolecular proton capture to compete successfully with intramolecular insertion (Scheme I).

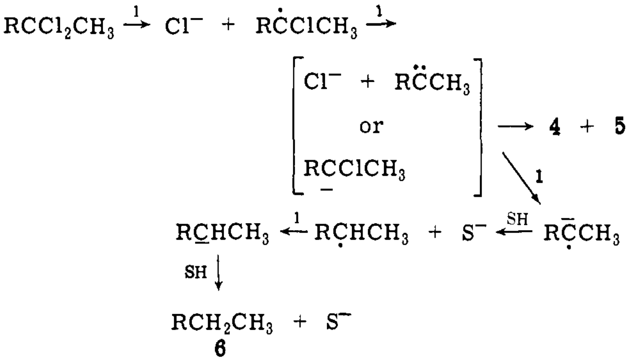
Scheme I



R = $(CH_3)_3C$
SH = dimethoxyethane

A possible alternative mechanism for the production of 3,3-dimethylbutane is outlined in Scheme II.

Scheme II



R = $(CH_3)_3C$
SH = dimethoxyethane

This rationale postulates that a free carbene (or carbenoid) can be reduced by sodium naphthalene (**1**) at a rate competitive with that of the intramolecular insertion reaction. This postulate derives some support from the observation that alkylcarbenes have been trapped on occasion, albeit very rarely, by intermolecular addition to olefins,[6] and from the fact that **1** reduces

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[6] For a recent comprehensive, authoritative review of carbene chemistry, see W Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

[7] W. Kirmse and B. G. v. Wedel, *Justus Liebigs Ann. Chem.*, **666**, 1 (1963); L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, 81, 5512 (1959).

simple alkyl free radicals at a rate at or near the diffusion-controlled limit.[5]

Fortunately a distinction between these two mechanisms can be readily achieved experimentally. If one focuses on the process by which the intermediates in the two mechanisms are diverted to carbene products (trimethylcyclopropane and *tert*-butylethylene) on the one hand and reduction product (2,2-dimethylbutane) on the other, one discerns a basic difference in the two mechanisms. In the mechanism presented in Scheme I, this partitioning takes place by divergent reactions of the carbenoid intermediate itself and is not dependent at the point of partition on further involvement of the reducing agent, **1**. More explicitly, the intermediate carbenoid is diverted from yielding carbenoid products by protonation, a reaction not dependent on radical anion concentration.[8] In the mechanism outlined in Scheme II, however, the carbene intermediate is diverted from conversion to carbene products only by further reduction, a process first order in sodium naphthalene (**1**) concentration.

Thus, Scheme I predicts that the ratio of carbene products to reduction product should be independent of the concentration of sodium naphthalene (**1**) employed, whereas Scheme II predicts that increasing the concentration of **1** should result in progressively higher yields of reduction product relative to carbene product. Experimentally, the mole ratio of 2,2-dimethylbutane to trimethylcyclopropane plus *tert*-butylethylene produced varied from 0.03 to 3.4 as the concentration ratio of 2,2-dichloro-3,3-dimethylbutane to sodium naphthalene employed was decreased from 10 to 0.1.[9] It is significant, furthermore, that over this entire range the ratio of *tert*-butylethylene to trimethylcyclopropane did not vary by more than 5%. These results, while inconsistent with the mechanism outlined in Scheme I, are wholly consistent with that set forth in Scheme II. Further evidence in refutation of Scheme I is provided by our failure to find any indication of the presence of 2-chloro-3,3-dimethylbutane in a reaction mixture to which insufficient sodium napththalene had been added to effect complete reduction of the starting dihalide.

Additional circumstantial evidence for the formation of carbene radical anions in the reaction of geminal dihalides with sodium naphthalene (**1**) derives from experiments conducted with the methylene halides as substrates. Since intramolecular carbene (carbenoid) products clearly result from reaction of **1** with both 2,2-dichloro-3,3-dimethylbutane and 1,1-dichloropropene, one would expect to be able to trap intermolecularly the methylene generated by reaction of **1** with a methylene halide. Reaction of CH_2Cl_2 with **1** in 40:60 (v/v) DME–cyclohexene does yield trace amounts of norcarane, but in no case have we been able to obtain this methylene addition product in greater than 0.4% yield. This result is explicable if the methylene generated is, in fact, reduced to the methylene radical anion H_2C^- at a rate rapid relative to that for addition of methylene to cyclohexene. The character and relative yield of the low molecular weight products which are formed in high yield in this reaction are wholly consistent with this hypothesis.[10]

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[8] This argument would be vitiated, of course, if 2-chloro-3,3-dimethylbutane were in rapid equilibrium with the carbenoid. This seems most unlikely, however, in the case of a simple alkyl chloride in the presence of the relatively weak bases (**1**, CH_3O^-) present in any significant concentration in the reaction medium.

[9] Since this reaction is macroscopically instantaneous, the significant variable is the mole ratio at the moment of mixing. The highest mole ratio of dihalide was obtained by injecting 4 ml of *ca.* 0.1 *M* **1** into 0.1 ml of 1 *M* dihalide solution. The lowest mole ratio of dihalide was obtained by injecting 3 ml of *ca.* 1 *M* **1** into 1 ml of 0.1 *M* dihalide solution. In this manner the volume of solvent and the number of moles of dihalide were held constant, and all reactions were carried to completion. Products **4**, **5**, and **6** were shown to be stable to excess sodium naphthalene.

[10] The details of this investigation will be described in a forthcoming publication.

[11] National Science Foundation Undergraduate Research Participant.

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Epimerization in the Preparation of Purine Nucleosides by the Fusion Reaction[1]

Sir:

Because of its convenience, the fusion reaction of Sato, *et al.*,[2] for the preparation of purine and pyrimidine nucleosides has gained favor over the established mercuri procedure of Davoll,[3] even though it is less stereospecific, often resulting in the formation of a significant quantity of the cis as well as the expected trans nucleosides[4–9] and, less frequently, of 7- as well as 9-glycosylpurines.[7,10]

We now wish to report the results of the acid-catalyzed fusion of a new *ribo*-hexofuranose with 2,6-dichloropurine. 1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranose (**1**)[11] was selectively hydrolyzed to 1,2-*O*-isopropylidene-α-D-allofuranose (**2**), which was oxidized with metaperiodate to 1,2-*O*-isopropylidene-α-D-*ribo*-pento-1,5-dialdo-1,4-furanose (**3**). Reaction of **3** with carbethoxymethylenephosphorane in tetrahydrofuran gave a mixture of *cis*- and *trans*-ethyl 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-heptofuran-5-enuronate (**4**), which was reduced with diimide to ethyl 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-heptofuranuronate (**5**). Treatment of **5** with acetic anhydride, glacial acetic acid, and concentrated sulfuric acid[12] gave, in an overall yield of 67% from **1**, ethyl 1,2,3-tri-*O*-acetyl-5,6-dideoxy-D-*ribo*-heptofuranuronate (**6**): nmr δ 1.25 (t, 3, CH_3CH_2O), 1.5–2.8 (m, 13, CH_2CH_2 and CH_3CO), 3.9–

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[1] This work was supported by funds from the C. F. Kettering Foundation, and Chemotherapy, National Cancer Institute, National Institutes of Health, Contract No. NIH-71-2021.

[2] T. Sato, T. Shimadate, and Y. Ishido, *Nippon Kagaka Zasshi*, **81**, 1440 (1960).

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[11] W. Sowa and G. H. S. Thomas, *Can. J. Chem.*, **44**, 836 (1966).

[12] Since Sowa[13] has recently reported that the use of 10 parts of acetic acid to 1 of acetic anhydride for the acetolysis of ribose caused epimerization to arabinose, we prepared **6** using a 1:1 mixture which was shown *not* to cause epimerization.

[13] W. Sowa, *Can. J. Chem.*, **49**, 3292 (1971).