survive long enough for collision and reaction with O_2 to dominate over rearrangement, and requires a radical lifetime $\geq 10^{-8}$ sec. A lifetime of $10^{-10.5}$ sec has been calculated for singlet trimethylene from the thermal isomerization of cyclopropane at 445°.[4c]

Earlier experiments conducted with ketene and ethylene in the presence of excess CO_2 indicated that cyclopropane:propylene ratios of 1.0 could be obtained at much lower pressures than that required for ketene–ethylene alone,[1c] and have been interpreted as resulting from very efficient collisional deexcitation of cyclopropane in the presence of CO_2. We have also observed relatively high values of f_Δ in our experiments ($f_\Delta = 0.83$ at 200 cm) with CO_2, but the tritium distribution ($f_a = 0.50 \pm 0.03$) indicates that the residual propylene-*t* has passed through a randomizing intermediate. These results are consistent with collisional conversion of ^{1}CHT to ^{3}CHT, followed by triplet reaction through the trimethylene-*t* intermediate, with only a small fraction of ^{1}CHT reaction in the system.

The ratio of insertion of ^{1}CHT into the C–H bond *vs.* reaction with the C=C bond is 0.08 ± 0.01 per bond. Previous estimates of a lower ratio (in the $^1CH_2$ system) have not taken the $^3CH_2$ contribution into account, as has been discussed earlier.[7]

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(3)-1,2-Dicarbollyl Complexes of Nickel(III) and Nickel(IV)

Sir:

We wish to report a new preparation of the (3)-1,2-dicarbollyl[1] sandwich complexes of iron[1-3] and cobalt,[4] $M^{n+}(B_9C_2H_{11})_2{}^{n-4}$ (M = Fe, Co). In addition, this preparative method has been employed in the preparation of similar species which contain nickel in the formal oxidation state of 2+, 3+, and 4+.

The $B_9C_2H_{12}^-$ ion, derived from 1,2-dicarbaclovododecaborane(12),[5] in hot aqueous sodium hydroxide solution (~40% by weight) was allowed to react with MCl_2 salts (M = Fe, Co, or Ni) to produce the complexes $Fe(B_9C_2H_{11})_2{}^{2-}$, $Co(B_9C_2H_{11})_2{}^-$, and $Ni(B_9C_2H_{11})_2{}^{2-}$, respectively. This preparation appears to involve the intermediate formation of the (3)-1,2-dicarbollide ion[1] by means of the following equilibrium.

$$B_9C_2H_{12}^- + OH^- \rightleftharpoons B_9C_2H_{11}^{2-} + H_2O$$

The $B_9C_2H_{11}^{2-}$ ion, generated *in situ*, may then react with the metal salts.[6] The M^{II} derivatives of iron and nickel were readily oxidized by air to the corresponding M^{III} species, while the Co^{II} complex disproportionated to form the Co^{III} complex and cobalt metal. All three M^{III} derivatives were isolated as their tetramethylammonium salts in up to 86% yield.

The $Fe^{III}(B_9C_2H_{11})_2{}^-$ and the $Co^{III}(B_9C_2H_{11})_2{}^-$ have been described previously.[2,4] Salts of newly discovered $Ni^{III}(B_9C_2H_{11})_2{}^-$ (I) are stable, brown [λ_{max} (ϵ): 237 (8500), 337 (21,000), and 435 (sh) mμ (3600)], and paramagnetic (μ_{eff} = 1.56 BM). *Anal.* Calcd for $(CH_3)_4NNi(B_9C_2H_{11})_2$: C, 24.14; H, 8.62; B, 48.97; N, 3.52; Ni, 14.76; formula wt, 398. Found: C, 24.02; H, 8.68; B, 49.35; N, 3.78; Ni, 14.48; formula wt, 399 (osmometric). I may be viewed as the (3)-1,2-dicarbollyl analog of nickelicinium ion. The oxidation of I in aqueous solution to the neutral species, $Ni^{IV}(B_9C_2H_{11})_2$ (II), required 1 equiv of $FeCl_3$. II is a diamagnetic yellow crystalline solid [λ_{max} (ϵ): 293 (18,000) and 425 mμ (1200)] which is stable in air, soluble in most organic solvents including saturated hydrocarbons, and sublimes *in vacuo* at 150°. *Anal.* Calcd for $Ni(B_9C_2H_{11})_2$: C, 14.83; H, 6.85; B, 60.18; Ni, 18.14; mol wt, 323. Found: C, 15.13; H, 6.85; B, 60.33; Ni, 17.84; mol wt, 309 (osmometric). High-resolution mass spectroscopy unequivocally verified the formulation $NiB_{18}C_4H_{22}$: calcd for $^{62}Ni^{11}B_{18}{}^{12}C_4{}^1H_{22}$, 330.268; found: 330.270. The ^{1}H nmr spectrum of II in benzene contained only a single resonance at τ 6.86 which was attributed to the carborane protons. The ^{11}B nmr spectrum of II closely resembled that of the isoelectronic $Co^{III}(B_9C_2H_{11})_2{}^-$ and $Fe^{II}(B_9C_2H_{11})_2{}^{2-}$. Polarography of II gave two reversible one-electron reductions at potentials +0.22 and − 0.63 v *vs.* sce. One equivalent of cadmium metal quantitatively reduced II to I while stronger reducing agents, *e.g.*, sodium amalgam, were required to convert I to $Ni^{II}(B_9C_2H_{11})_2{}^{2-}$. These data strongly support our formulation of I and II as Ni^{III} and Ni^{IV} complexes, respectively.

At the present time, very few well-characterized Ni^{III} and Ni^{IV} compounds have been described,[7a,b] and these species may be roughly divided into three classes. One class comprises the complex oxides and fluorides, and a second class contains complexes with bidentate ligands which employ phosphorus, arsenic, sulfur, or nitrogen as donor stoms.[8] Finally, the third class is exemplified by the $Ni^{III}(C_5H_5)_2{}^+$ (nickelicinium) ion[9] which resists oxidation[10] to the dipositive complex, $Ni^{IV}(C_5H_5)_2{}^{2+}$. The new Ni^{III} and Ni^{IV} complexes described in this communication appear to fall in the third class and may have the sandwich structure of the other known (3)-1,2-dicarbollyl complexes.

The chemistry and structures associated with the nickel system are currently under investigation, and the results of these studies will be reported in full at a later data.

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[1] M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965), present the nomenclature system employed for these species and the $B_9C_2H_{11}{}^{2-}$ dicarbollide ions.

[2] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965).

[3] A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

[4] M. F. Hawthorne and T. D. Andrews, *Chem. Commun*, 443 (1965).

[5] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[6] The possibility exists that the $B_9C_2H_{12}^-$ ion actually complexes with the metal ion in the first step of the reaction followed by proton abstraction by OH^- in a subsequent step.

[7] (a) For a review on the subject, see R. S. Nynolm, *Chem. Rev.*, **53**, 263 (1953), and references therein; (b) B. N. Figgis and J. Lewis [*Progr. Inor. Chem.*, **6**, 195 (1964)] discuss magnetic properties.

[8] As an example, see E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965), for a recent series of references.

[9] G. Wilkinson, P. L. Pauson, J. M. Birmingham, and F. A. Cotton, *ibid.*, **75**, 1011 (1953).

[10] G. Wilkinson, P. L. Pauson, and F. A. Cotton, *ibid.*, **76**, 1970 (1954).

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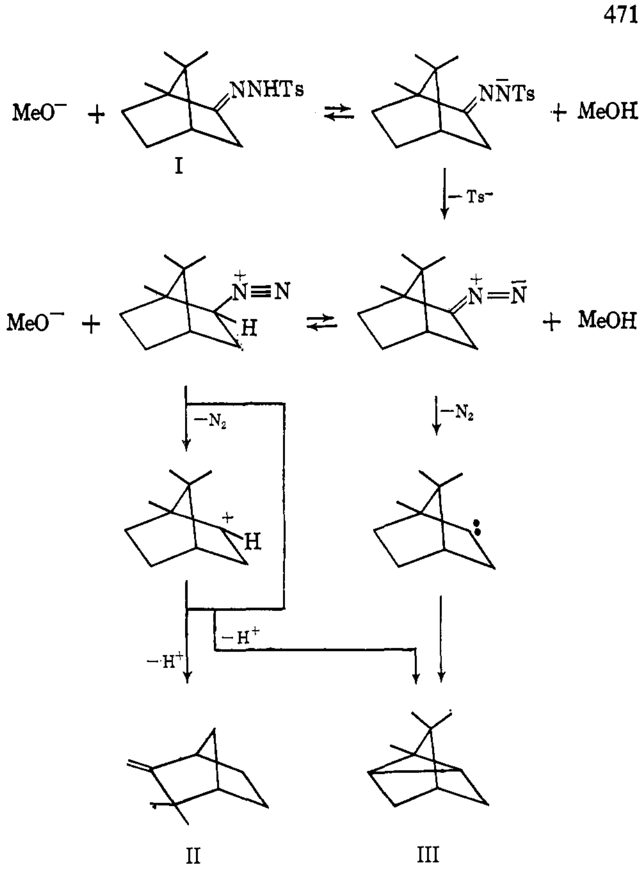
An Investigation of the Intermediates in the Base-Catalyzed Decomposition of Camphor Tosylhydrazone in Aprotic Solvents

Sir:

We have recently investigated the effect of trivalent metal cations on the camphene:tricyclene ratio resulting from the base-catalyzed decomposition of camphor tosylhydrazone (I) in aprotic solvents.[1] The results of this investigation led us to conclude that the trivalent metal cation participates in the formation of an intermediate which behaves like a 2-bornyl cation and rearranges to camphene (II). The formation of tricyclene (III) was assumed to arise from a carbene intermediate *via* a transannular carbon–hydrogen insertion reaction, as has been reported in many investigations.[2]

We have been studying the effect of base concentration on the decomposition of camphor tosylhydrazone (I) with sodium methoxide and sodium hydride in aprotic solvents[3] and have obtained strong evidence that the nature of the intermediate which leads to tricyclene (III) is dependent upon the relative amount of base present in the reaction mixture.

In the base-dependence study[3] we discovered that the relative amount of camphene (II) to tricyclene (III) decreased at higher base concentrations. Friedman, *et al.*, made a similar observation in the decomposition of cyclopropanecarboxaldehyde tosylhydrazone with sodium methoxide.[4] When less than 1 equiv of base was used or when the reaction was run in ethylene glycol, bicyclobutane, presumably arising from a carbonium ion intermediate, was the major product.[4] Wiberg and Lavanish studied the decomposition of cyclopropanecarboxaldehyde tosylhydrazone in protic solvents and also concluded that the bicyclobutane was generated from a cationic intermediate.[5]



We allowed camphor tosylhydrazone (I) to decompose with 0.75, 2.00, and 4.00 equiv of sodium methoxide in diglyme in the presence of deuterium oxide (40 equiv). The camphene (II) and tricyclene (III) formed in the reaction were separated and collected by gas chromatography. The collected samples were split; half of the material was reinjected into the gas chromatograph as a check for purity, and the other half was submitted for mass spectral analysis. The camphene (II) from each reaction mixture contained 80 ± 2% d_1, the remainder being unlabeled. The tricyclene (III) from the 0.75-equiv reaction contained 64% d_1, that from the 2.00-equiv reaction 25% d_1, and that from the 4.00-equiv reaction 8% d_1. The first result is consistent with that obtained by Wiberg, who obtained labeled bicyclobutane from the decomposition of cyclopropanecarboxaldehyde tosylhydrazone with less than 1 equiv of base in ethylene glycol-d_2.[6]

Tricyclene (III) formation by way of a carbene does not lead to the incorporation of a deuterium atom, and therefore it is clear that with 0.75 equiv of sodium methoxide about two-thirds of the III is generated from some other intermediate, whereas at higher concentrations (*e.g.*, 4.00 equiv) the carbene mechanism appears to predominate. A cationic mechanism is consistent with deuterium incorporation at low base concentrations, and in fact the cationic formation of tricyclene is in complete accord with the report that bicyclobutane results from a cationic intermediate in the base-catalyzed decomposition of cyclopropanecarboxaldehyde tosylhydrazone.[4,5] These results are also consistent with other reports of cyclopropane formation from cationic intermediates,[7] especially those describing the formation of nortricyclene from the norbornyl cation[8] and norbornanediazonium ion[9] in protic solvents. However, in the base-catalyzed decomposition of camphor tosylhydrazone (I) the generated cyclopropane, III, can be formed from one of two intermediates depending on the concentration of base.

Considering first the decomposition of I with 0.75 equiv of base, the following explanation is consistent

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[1] R. H. Shapiro, *Tetrahedron Letters*, 3401 (1966).

[2] See W. Kirmse, "Carbene Chemistry," Academic Press Inc., New N. Y., 1964, Chapter 3, for a review.

[3] R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Am. Chem. Soc.*, in press.

[4] J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **87**, 659 (1965).

[5] K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 365 (1966).

[6] Personal communication from Professor Wiberg, Aug 11, 1966. See K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 5272 (1966); F. Cook, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).

[7] W. Hückel and G. Meinhardt, *Ber.*, **90**, 2025 (1957); G. M. Komppa and G. A. Nyman, *Ann.*, **535**, 252 (1938); M. Bredt-Savelsberg, *Ber.*, **56**, 554 (1923); G. Wagner, S. Moycho, and F. Zienkowski, *ibid.*, **37**, 1032 (1904).

[8] S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965).

[9] A. Nickon and N. H. Werstiuk, *ibid.*, **88**, 4543 (1966).