potassium carbonate followed by reduction with lithium aluminum hydride to the alcohol.

Acetone was reduced with lithium aluminum deuteride to give 2-propanol-2-d_1 followed by treatment with phosphorus tribromide to give 2-bromopropane-2-d_1.[4] Part of the 2-bromopropane-2-d_1 was allowed to react, *via* the Grignard reagent, with 2-methylpropanal to give 2,4-dimethyl-3-pentanol-2-d_1 and part of the 2-bromopropane-2-d_1 was allowed to react, *via* the Grignard reagent, with ethyl formate to give 2,4-dimethyl-3-pentanol-2,4-d_2. The brosylates of the various alcohols were prepared by the usual Tipson procedure.[5]

The nmr analysis of the starting bromoethane-1,1-d_2 as well as the I-d_2 indicated that this alcohol was 98.7% β d_2. Nmr analysis of the I-d_4 indicated that this alcohol was 99.4% β d_4.

The nmr analysis of the II-d_1 and II-d_2 compounds showed them to be 100% β d_1 and d_2, respectively. This was to be expected since they were prepared from the same sample of 2-bromopropane-2-d_1 which showed no trace of α hydrogens according to nmr analysis. Nmr analysis of the brosylates likewise showed 100% d_1 and d_2, respectively, when prepared from these alcohols.

The rate data, shown in Table I, were obtained by the precise conductometric determination[6] of the first-order solvolysis rate constants of the brosylates in 70 vol % aqueous ethanol at 25°. The precision of the conductometric method is ±0.05%.

Table I. Solvolysis Data[a] for 3-Pentyl- and 2,4-Dimethyl-3-pentyl Brosylates

Compound	$K_1 \times 10^5$ sec^{-1}	K_H/K_D
$CH_3CH_2CHOBsCH_2CH_3$	5.9736	
$CH_3CD_2CHOBsCH_2CH_3$	4.5353	1.3171
$CH_3CD_2CHOBsCD_2CH_3$	3.4400	1.7365
$CH(CH_3)_2CHOBsCH(CH_3)_2$	9.3472	
$CD(CH_3)_2CHOBsCH(CH_3)_2$	6.8372	1.3671
$CD(CH_3)_2CHOBsCD(CH_3)_2$	4.4134	2.1179

[a] In 70 vol % ethanol–water at 25°. K corrected to 100% deuterium content.

For the case of the 3-pentyl brosylates, the data show that successive deuterium substitution leads to cumulative isotope effects, *i.e.*, the solvolytic rate retardation caused by the tetradeuteration equals the square of that caused by monodeuteration: $(\text{I-}d_4) = 1.7365 \cong 1.7348 = (1.3171)^2 = (\text{I-}d_2)^2$. This cumulative behavior observed for β-deuterium isotope effects is best explained by hyperconjugation.[7]

However, in the case of the 2,4-dimethyl-3-pentyl brosylates, the successive deuterium substitution does not lead to cumulative isotope effects; *i.e.*, the rate retardation caused by dideuteration does not equal the square of that caused by monodeuteration: $(\text{II-}d_2) = 2.1179 \neq 1.8690 = (1.3671)^2 = (\text{II-}d_1)^2$. The effect of each β-deuterium atom in the solvolytic transition state may be calculated using the expression of the form[7] $(K_H/K_D)_x = 2xx'/(x + x')$ where $(K_H/K_D)_x$ is the experimentally determined isotope effect for substitution of a single deuterium atom while x and x' are the effects of the first and second deuterium atoms in the transition state. This type of analysis leads to the isotope effects of 1.018 and 2.080 for the replacement of the first and second β hydrogens in 2,4-dimethyl-3-pentyl brosylates. As was suggested in the case of the *cis*-4-*t*-butylcyclohexyl brosylate,[1] this noncumulative isotope effect behavior is best explained in terms of neighboring participation in the solvolytic transition state. This is contrasted with the cumulative isotope effects for the 3-pentyl system which are attributed to hyperconjugation.

The K_H/K_D of 2.12 (Table I) for II-d_2 is very close to the K_H/K_D of 2.15 observed for 3-methyl-2-butyl-3-d tosylate reported by Winstein and Takahashi.[8]

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(4) V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **74**, 5285 (1952).

(5) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(6) B. L. Murr and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **84**, 4672 (1962).

(7) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *ibid.*, **85**, 2413 (1963).

(8) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

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Thermal and Photo [3,3] Sigmatropic Rearrangements in the *cis*-2,2-Dimethyl-3-isobutenylcyclopropyl Isocyanate–3,6-Dihydro-3,3,6,6-tetramethyl-2H-azepin-2-one System[1]

Sir:

In a previous paper[2] we have shown that *cis*-2,2-dimethyl-3-isobutenylcyclopropyl isocyanate (**2**) is stable in refluxing benzene, in contrast with the thermal instabilities of *cis*-2-vinylcyclopropyl isocyanate (**9**)[3a,b] and *exo*- and *endo*-benzonorcaradienyl isocyanate[3c] under similar conditions.

We wish to report in this communication the thermal [3,3] sigmatropic rearrangement (the Cope rearrangement) of **2** which afforded a novel aza analog of homocyclohexadienone (ii), **3** (3,6-dihydro-3,3,6,6-tetramethyl-2H-azepin-2-one), having a very reactive imino ketone structure, and also the photo [3,3] sigmatropic rearrangement of **3** to **2**.

Pure **2**, bp 90° (20 mm), obtained by the Curtius rearrangement of the corresponding *cis*-azide **1**, was heated in dry *o*-xylene at the refluxing temperature (144°) for 60 hr, affording an equilibrium mixture of **2** and a product (**3**) in the ratio of 1:7 (glpc analysis). Distillation under reduced pressure (2 mm) gave a

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(1) Studies on Chrysanthemic Acid. V. Part IV: T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, **35**, 790 (1970).

(2) T. Sasaki, S. Eguchi, and M. Ohno, *Tetrahedron*, **25**, 2145 (1969).

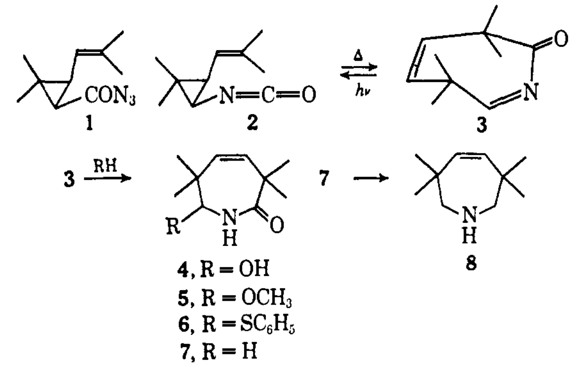
(3) (a) E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Justus Liebigs Ann. Chem.*, **682**, 1 (1965). (b) The intermediate formation of **9** in the decomposition of *cis*-2-vinylcyclopropyl carbonyl azide has been demonstrated recently; **9** underwent Cope rearrangement to 2,3-dihydro-1H-azepin-2-one (**11**) rapidly at room temperature: I. Brown, O. E. Edwards, J. M. McIntosh, and D. Vocelle, *Can. J. Chem.*, **47**, 2751 (1969). (c) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

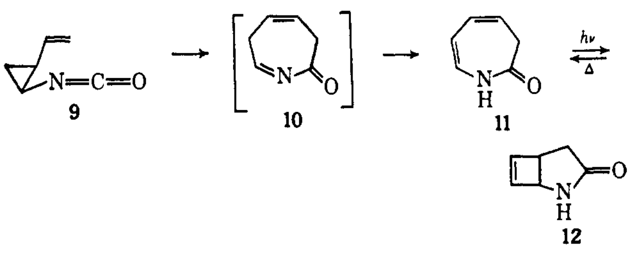
Table I. Spectral Data of **3**–**8**

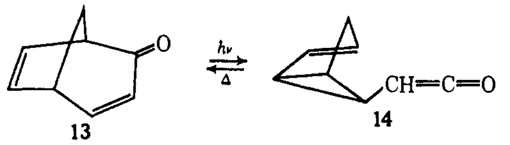
	Ir, cm^{-1} [b]			Nmr, τ (J, Hz) [c]					Uv, nm (ϵ) [d]	
Compd [a]	C=O	C=C	Others	-CH=CH-	C_7–H	CH_3	NH	Others	λ_{max}	End
3	1710	1645 755	1665 (C=N)	4.72 (d, 12) 4.95 dd. 12, 1.5)	2.49 (d. 1.5)	8.77 (s)			288 (255)	210 (1670)
4	1620 [e]	750	3220 (OH,NH)	4.64 (d, 12.5) 4.86 (d, 12.5)	5.93 (s)	8.67 (s) 8.93 (s)	3.40 (br s)	5.02 (br s, OH)		210 (2200)
5	1655 [e]	755	3220 (NH) 1095 (C—O)	4.72 (d, 12) 4.95 (d, 12)	5.93 (d, 6)	8.72 (s) 8.93 (s)	1.62 (d, 6)	6.57 (s, OCH_3)		
6	1640 [e]	750	3180 (NH) 1580 1475 (C_6H_5)	4.57 (d, 12) 4.83 (d, 12)	5.08 (d, 6)	8.71 (s) 8.84 (s)	3.83 (br d)	2.70– 2.90 (m, C_6H_5)		
7	1640 [e]	750	3200 (NH)	4.54 (d, 12.5) 4.78 (d, 12.5)	6.76 (d, 7)	8.63 (s) 8.97 (s)	2.95 (br d)		205 (6350)	
8		1655 755	3300 (NH)	4.88 (s)	7.33 (s)	9.00 (s)	6.96 (s)			

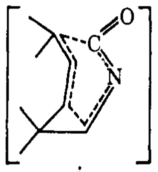
[a] All compounds had satisfactory analyses. [b] In KBr for solids and neat for liquids. [c] Nmr spectra of **3**, **5**, and **8** were obtained in CCl_4, and those of **4**, **6**, and **7** in $CDCl_3$ at 60 MHz. Areas of each signal were compatible with the assigned structures. [d] **3** and **7** in cyclohexane, and **4** in ethanol. [e] Superimposed with C=C.

colorless oil (**3**), bp 79° (60% yield), together with recovered isocyanate, bp 50–55° (8.5% recovery). The ir spectrum of **3** showed no NCO absorption at 2270 cm^{-1},[2] though the analysis and the mass spectral parent ion peak at *m/e* 165 indicated the same molecular formula of $C_{10}H_{15}ON$ as the isocyanate. The structure of **3** was determined as 3,6-dihydro-3,3,6,6-tetramethyl-2H-azepin-2-one, the Cope rearrangement product, on the basis of the spectral (Table I) and chemical properties (described below). The characteristic absorption bands in the ir spectrum suggested the presence of an imino ketone moiety (1710 and 1665 cm^{-1})[4] and an olefin (1645 and 755 cm^{-1}). In the nmr spectrum, the presence of a long-range coupling between C_5–H and C_7–H was indicative of the W configuration of H–C_5–C_6–C_7–H.[5] In the mass spectrum, appearance of an ion peak at *m/e* 110 due to a 2,5-dimethyl-2,4-hexadiene fragment as the base peak supported the assigned ring structure.

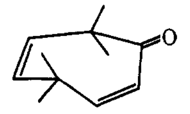








i



ii

3 showed the characteristic imino ketone reactivity[3a] to nuceophiles such as water, methanol, and thiophenol leading to the quantitative formation of the corresponding adducts **4**, mp 144–145°, **5**, an oil, and **6**, mp 102–103°, respectively. Catalytic hydrogenation of **3** in cyclohexane with Adams catalyst afforded an ε-lactam, **7**, mp 113–114°, in quantitative yield. Reduction of **3** with excess lithium aluminium hydride in dry ether at room temperature overnight afforded 40% yield of **7** and 60% of an oily amine, **8** (picrate mp 142–143°), which was characterized as 2,3,6,7-tetrahydro-3,3,6,6-tetramethyl-1H-azepine. The difficult hydrogenation of the double bond in **3** can be rationalized by steric hindrance due to the presence of two *gem*-dimethyl groups at C_3 and C_6, which apparently cause ring stabilization of the so far unknown new ring systems in **3** and in **8**. The structural assignments of

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(4) K. Tsuda and R. Hayatsu, *J. Amer. Chem. Soc.*, **78**, 4107 (1956).

(5) For a recent review on the spin-spin coupling constants, see S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

4–8 rest on the analytical and spectral data (Table I). All of these products had a common base ion peak at *m/e* 110 as one of the characteristic mass spectral fragmentations.

In order to examine the photochemical behavior, **3** was irradiated in cyclohexane with a 100-W high-pressure mercury lamp at room temperature for 50 hr until **3** completely disappeared on glpc. The identified main product was the isocyanate **2** (20% yield),[6] while under similar conditions **2** remained mostly unchanged.[7] These results indicate that a photolytic conversion of **3** to **2** is possible which is different from that of known photovalence isomerization of **11** to **12**,[3a] but is quite similar to the homoelectrocyclic reaction reported recently for several bicyclic dienones such as **13**,[8] where the formation of cyclopropylketene **14** is photochemically favored, while that of **13** is thermally favored

It should be mentioned here that considerable steric repulsion between a *flagpole* methyl group and one of the methyl groups on the cyclopropyl ring might be involved in the boatlike transition state i[9] due to the geometrical constraint of **2** and **3** prohibiting [3,3] sigmatropic rearrangements, and, therefore, the **2** → **3** conversion proceeds only under energetic conditions (144°) compared to the mild ones (even room temperature) for the **9** → **10** → **11** conversion.[3a,b,10]

(6) Several other products were produced, but they have not been identified yet.

(7) **3** in cyclohexane was stable in dark at room temperature.

(8) (a) O. L. Chapman, M. Kane, J. D. Lassile, R. L. Loeschen, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6856 (1969), and references therein; (b) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969), in which photochemistry of homocyclohexadienone (ii) has been described.

(9) For a recent review on the Cope rearrangement, see H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 111 (1969); see also M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968), and references therein.

(10) For the facile valence isomerization of *cis*-2-vinylcyclopropanecarboxaldehyde, see S. J. Rhoads and R. D. Cockroft, *ibid.*, **91**, 2815 (1969).

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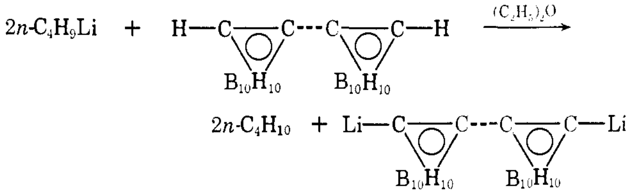
Novel Chelated Biscarborane Transition Metal Complexes Formed through Carbon–Metal σ Bonds

Sir:

Numerous π-bonded transition metal complexes with $B_9C_2H_{11}{}^{2-}$, $B_7C_2H_9{}^{2-}$, and $B_6C_2H_8{}^{2-}$ ligands have recently been reported.[1–8] In addition, a few examples of neutral σ-bonded transition metal complexes involving single carbon–transition metal bonds have been described.[9,10] We now wish to report the first example of anionic transition metal complexes which contain a novel chelating carborane group and unusually stable carbon–metal σ bonds.

Reaction of biscarborane [1-(1′,2′-dicarba-*closo*-dodecaborano(12))-1,2-dicarba-*closo*-dodecaborane(12)] with 2 equiv of *n*-butyllithium in ethyl ether affords *n*-butane and a slurry of 2,2′-dilithiobiscarborane.[11] Treatment of this ether slurry with



1 equiv of anhydrous $CuCl_2$ at reflux for 3 hr, followed by cation exchange with 0.5 mol equiv of $(C_2H_5)_4NBr$ in CH_2Cl_2, elution of the product from a short silica gel column with 50:50 $(C_2H_5)_2O$–CH_2Cl_2, and recrystallization from CH_2Cl_2–C_6H_{14} yields 52% of a diamagnetic yellow crystalline solid, $[(C_2H_5)_4N]Cu^{III}[(B_{10}C_2H_{10}{}^-)_2]_2$, mp 210–212° (I). Elemental analyses and molecular weights were satisfactory for I and all other complexes. The 32.1-MHz ^{11}B nmr spectrum of I consisted of two sets of overlapping resonances centered at +3.9 and −0.5 ppm, respectively, relative to $BF_3 \cdot O(C_2H_5)_2$. The 60-MHz ^1H nmr spectrum of I in deuterioacetone exhibited cation resonances centered at τ 8.60 (triplets of triplets, intensity 3) and 6.52 (quartet, intensity 2). The infrared spectrum of I as a Nujol mull contained absorptions at 2500 (s), 1170 (s), 1072 (s), 1030 (m), 999 (m), 928 (w), 782 (m), 735 (sh), and 725 cm^{-1} (s). The electronic spectrum of I in CH_3CN exhibited maxima at 374 (ε 28,400), 272 (ε 14,000), and 200 mμ (sh, ε 9000).

Reduction of I with lithium in acetone containing $(C_2H_5)_4NBr$, followed by fractional crystallization of the product, gave blue needles of $[(C_2H_5)_4N]_2Cu^{II}[(B_{10}C_2H_{10}{}^-)_2]_2$, mp 221–223° (II), in 55% yield. The magnetic moment of solid II was 1.8 BM. The infrared spectrum of II as a Nujol mull showed absorptions at 2520 (s), 1185 (s), 1052 (sh), 1030 (m), 1000 (s), 956 (w), 851 (w), 785 (s), 732 (s), and 725 cm^{-1} (sh). The electronic spectrum of II in CH_3CN exhibited maxima at 552 (ε 1030), 334 (ε 13,000), and 271 mμ (ε 40,000). Cyclic voltammetry of I or II in CH_3CN with $(C_2H_5)_4NClO_4$ as the supporting electrolyte gave a reversible wave at +0.15 V *vs.* sce for the $Cu^{3+}|Cu^{2+}$ couple and an irreversible wave at −1.36 V for an apparent $Cu^{2+}|Cu^+$ couple.

Treatment of 2,2′-dilithiobiscarborane with 0.5 mol equiv of anhydrous $NiBr_2$[12] as an ether slurry for 3 hr gave a red-brown oil, which dissolved in dry CH_2Cl_2 containing 1 mol equiv of $(C_2H_5)_4NBr$. Addition of ether precipitated an orange-brown solid which was recrystallized twice from CH_2Cl_2. Bright orange plates of diamagnetic $[(C_2H_5)_4N]_2Ni^{II}[(B_{10}C_2H_{10}{}^-)_2]_2$, mp 259–262° (III), were obtained in 58% yield. The 32.1-MHz ^{11}B nmr spectrum of III contained overlapping resonances centered at +7.2 ppm. The 60-MHz ^1H nmr spectrum of III in deuterio-

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(1) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

(2) M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967).

(3) M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).

(4) T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968).

(5) J. N. Francis and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968).

(6) M. F. Hawthorne and H. R. Ruhle, *Inorg. Chem.*, **8**, 176 (1969).

(7) T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 5475 (1969).

(8) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(9) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, **20**, 1205 (1968).

(10) J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1031 (1969).

(11) J. A. Dupont and M. F. Hawthorne, *ibid.*, **86**, 1643 (1964).

(12) R. B. King, Ed., "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, p 72.