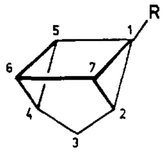
Communications to the Editor

On the Intermediacy of Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]hept-1(7)-ene, a Highly Strained Bridgehead Olefin

Sir:

Recently evidence has been accumulated that tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene and related bicyclo[1.1.0]but-1(3)-ene derivatives are formed as fleeting intermediates, when the corresponding bridgehead-halogen-substituted bicyclo[1.1.0]butanes are treated with a strong base.[1] We now report our preliminary results on the quadricyclane[2] system which indicate that the title compound might be a short-lived species, generated by the base treatment of 1-chloroquadricyclane (**1c**).

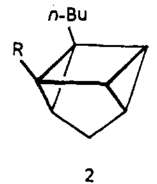


1:	a	b	c	d
R:	H	Li	Cl	n-Bu

The synthesis of **1c** was achieved by metalating quadricyclane (**1a**)[3] with the *n*-butyllithium–tetramethylethylenediamine complex to **1b** (in *n*-hexane, 24 h at 20 °C) and chlorinating **1b** with *p*-toluenesulfonyl chloride[4] (yield 44%). Structure proof for **1c** rests on its ^{13}C NMR spectrum ((CDCl$_3$) δ 14.04 (d), 23.65 (d), 24.92 (d), 26.97 (d), 31.23 (t), 31.73 (d), 45.77 (s)), its mass spectrum (*m/e* 126, 128 (M$^+$)), and its facile conversion to 2-chloronorbornadiene,[5] either thermally at 140 °C (in C$_6$D$_6$, sealed NMR tube), or by catalysis with a trace of silver trifluoromethylsulfonate at 20 °C.

When **1c** was mixed with *n*-butyllithium in ether, 1-*n*-butylquadricyclane (**1d**) was formed in a 62% yield. The structure of **1d** is based on its ^{13}C NMR spectrum ((CDCl$_3$) δ 13.41 (d), 14.10 (q), 17.51 (d), 18.21 (d), 22.63 (d), 24.50 (d), 27.73 (t), 27.96 (s), 28.69 (t), 29.68 (t), 30.80 (t)), its mass spectrum (*m/e* 148 (M$^+$)), and its thermal transformation to 2-*n*-butylnorbornadiene.[6]

Some insight into the mechanism of the reaction **1c** → **1d** was gained by mixing **1c** with *n*-butyllithium and, subsequently, adding methyl bromide to the reaction mixture. The isolated *n*-butylmethylquadricyclane fraction (30% yield) was composed of **2b** and **3b** in a 2:1 ratio. The composition of this mixture was determined by gas chromatography and by ^{1}H NMR spectroscopy after thermal conversion of **2b** and **3b** to **5** and **6**, respectively.[7] Significantly, the isomer **4b** (and **7**) was not formed in this reaction.



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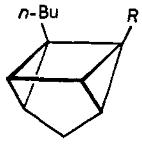

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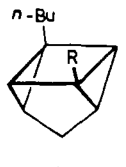

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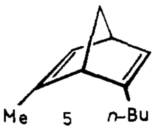
a: R = Li
b: R = Me



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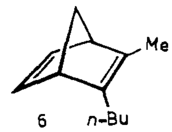

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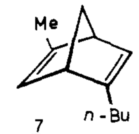

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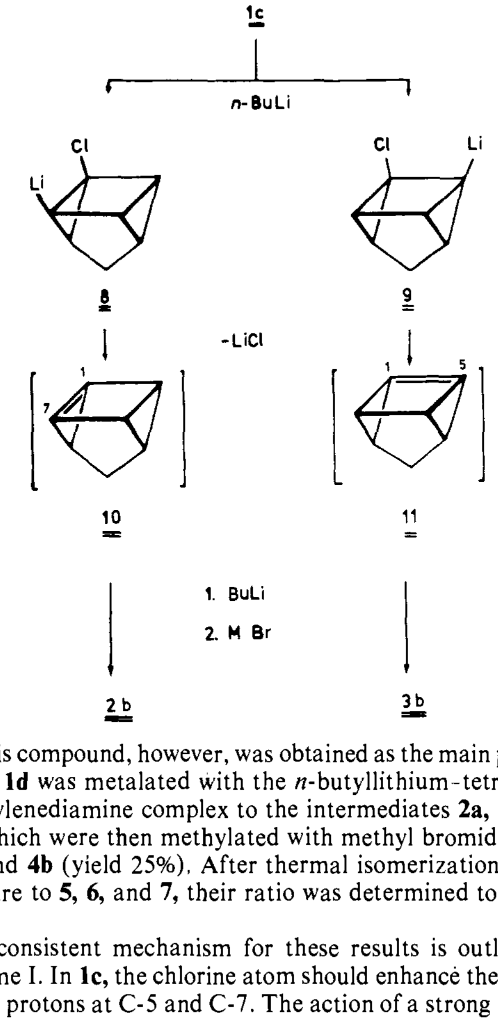
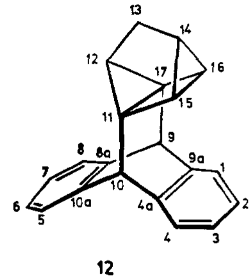
Scheme I



This compound, however, was obtained as the main product when **1d** was metalated with the *n*-butyllithium–tetramethylethylenediamine complex to the intermediates **2a**, **3a**, and **4a**, which were then methylated with methyl bromide to **2b**, **3b**, and **4b** (yield 25%). After thermal isomerization of this mixture to **5**, **6**, and **7**, their ratio was determined to be 1:1:1.7.

A consistent mechanism for these results is outlined in Scheme I. In **1c**, the chlorine atom should enhance the acidity of the protons at C-5 and C-7. The action of a strong base on **1c** should then lead via **8** or **9** to the intermediate dehydroquadricyclanes **10** and **11**, which would be trapped by the excess of the base.

To test this scheme, **1c** was added to a mixture of anthracene and lithium 2,2,6,6-tetramethylpiperidide in THF in the range of 20–60 °C. The product, isolated in a yield of 35–45% (mp 125 °C dec from toluene), was identified as 9,10-dihydro-9,10-(1,7-tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptano)anthracene (**12**), the Diels–Alder adduct of **10** and anthracene. The structure followed from the mass spectrum (*m/e* 268 (M$^+$)), the ^{1}H NMR spectrum ((CDCl$_3$) δ 1.01–1.55 (m, 4 H), 1.98 (t, J = 1.5 Hz, 2 H), 4.43 (s, 2 H), 7.05–7.50 (m, 8 H)), and the ^{13}C NMR spectrum ((CDCl$_3$) δ 12.81 (d), 22.87 (d), 28.84 (s), 33.47 (t), 40.60 (d), 45.12 (d), 123.59 (d), 124.62 (d), 125.31



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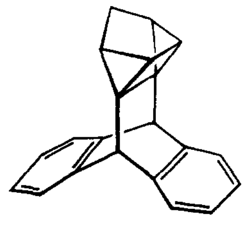

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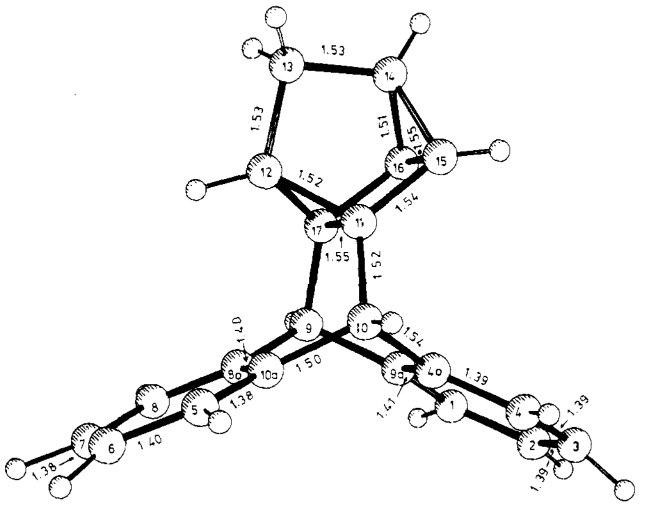

Figure 1. A perspective view of **12**. Values for the CC bond lengths (ångstroms) are displayed.

Table I. Selected CCC Bond Angles of **12**

∠C-C-C	degree	∠C-C-C	degree
9-17-11	113	11-15-14	104
9-17-12	125	12-13-14	100
9-17-16	128	13-14-16	111
11-12-17	60	14-15-16	58
11-17-12	60	15-14-16	62
11-15-16	90	15-11-17	89

(d), 125.74 (d), 141.26 (s), 144.71 (s)). The latter excludes **13**, the Diels-Alder adduct of **11** and anthracene, the ^{13}C NMR spectrum of which should show only five different signals for aliphatic C atoms.[8]

The X-ray analysis of the Diels-Alder adduct definitely proved structure **12** which is depicted in detail in Figure 1. Selected bond angles are given in Table I.[9]

Note that the bond C-11-C-17 is the central bond of a [4.2.1]propellane system. Furthermore, the centers of the propellane subunit, C-11 and C-17, show the phenomenon of the "inverted tetrahedron".[10,11]

The outcome of the trapping experiment with the formation of the adduct **12** is in accordance with Scheme I. However, at present it is not clear why the expected isomer **13** could not be detected. Attempts are underway to establish fully the intermediacy of the proposed reactive species **10** and **11.**

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References and Notes

(1) (a) G. Szeimies, J. Harnisch, and O. Baumgärtel, *J. Am. Chem. Soc.*, **99,** 5183 (1977); (b) G. Szeimies, J. Harnisch, and K.-H. Stadler, *Tetrahedron Lett.*, 243 (1978); (c) U. Szeimies-Seebach and G. Szeimies, *J. Am. Chem. Soc.*, **100,** 3966 (1978); (d) J. Harnisch, H. Legner, U. Szeimies-Seebach, and G. Szeimies, *Tetrahedron Lett.*, 3683 (1978); (e) U. Szeimies-Seebach, J. Harnisch, G. Szeimies, M. Van Meerssche, G. Germain, and J.-P. Declercq, *Angew. Chem., Int. Ed. Engl.*, **17,** 848 (1978).

(2) IUPAC name: tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane. S. J. Cristol and R. L. Snell (*J. Am. Chem. Soc.*, **80**, 1950 (1958)) coined this ring system "quadricyclene", which most, but not all, users silently changed to "quadricyclane" (H. Hogeveen and B. J. Nusse, *ibid.*, **100,** 3110 (1978); Y. Sugiyama, T. Kawamura, and T. Yonezawa, *ibid.*, **100,** 6525 (1978); T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *ibid.*, **99,** 871 (1977); D. S. Kabakoff, J.-C. G. Bünzli, J. F. M. Oth, W. B. Hammond, and J. A. Berson, *ibid.*, **97,** 1510 (1975); R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *ibid.*, **97,** 812 (1975); H. K. Hall, Jr., C. D. Smith, and J. H. Bald, *ibid.*, **95,** 3197 (1973)). Here, we follow this latter practice. On this basis, **10** and **11** could be named 1,7- and 1,5-dehydroquadricyclane, respectively.

(3) C. D. Smith, *Org. Synth.*, **51,** 133 (1971).

(4) G. Szeimies, F. Philipp, O. Baumgärtel, and J. Harnisch, *Tetrahedron Lett.*, 2135 (1977).

(5) D. I. Davies, *J. Chem. Soc.*, 3669 (1960).

(6) The spectral data of this compound are consistent with the proposed structure.

(7) The norbornadienes **5, 6**, and 7 were separated by preparative GLC (20% Carbowax 20M on Kieselguhr; retention times for **5**–7 were in the order **6** $<$ 7 $<$ **5**) and the compounds were identified by the chemical shifts of the olefinic and bridgehead protons in the respective ^{1}H NMR spectra ($CDCl_3$, δ scale): **5,** 6.04 (narrow m, 2 H), 2.90 (narrow m, 1 H), 3.25 (narrow m, 1 H); **6,** 6.63 (narrow m, 2 H), 3.09 (narrow m, 1 H), 3.17 (narrow m, 1 H); 7, 6.01 (narrow m, 2 H), 3.04 (m, 2 H).

(8) Judging from the NMR spectra of the raw material, **13** could not have been formed in a yield $>$5%.

(9) Space group $P2_1/n$; $Z = 8$; a = 18.407 (19), b = 14.244 (5), c = 11.153 (10) Å; β = 105.99 (7)°. The intensities of 4159 reflexions were measured on a Syntex P2$_1$ automated diffractometer (Mo Kα radiation; $2\theta_{max} = 47°$) and 1293 were used for the resolution with the program MULTAN 77 (P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J.-P. Declercq, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, England, and University of Louvain-la-Neuve, Belgium) and refined to R = 0.075 with the X-RAY 72 SYSTEM (Technical Report TR-192. Computer Science Center, University of Maryland, College Park, 1972).

(10) K. B. Wiberg, G. J. Burgmaier, K. W. Shen, S. J. La Placa, W. C. Hamilton, and M. D. Newton, *J. Am. Chem. Soc.*, **94,** 7402 (1972); C. S. Gibbons and J. Trotter, *Can. J. Chem.*, **51,** 87 (1973).

(11) The distance of C-11 to the nearest tetrahedral plane (C-10–C-12–C-15) is 0.05 Å. This plane intersects the C-11–C-17 bond.

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Disproportionation of a Neutral Metal-Formyl Complex and Synthesis of a Stable Hydroxymethyl-Metal Compound

Sir:

The projected petroleum shortage has caused renewed interest in alternative sources of liquid fuels and petrochemical feedstocks. One such alternative that is now being widely investigated is the reduction of coal-derived carbon monoxide-hydrogen mixtures via the Fischer-Tropsch and related reactions.[1] Little is known, however, about the course of these reactions, and proposed mechanisms are essentially only intelligent speculations. For the past several years, we have been studying some of the unusual intermediates and reactions which have been proposed to occur in CO reduction.[1-3] We,[1,2] and others,[4] have synthesized and studied the reactions of metal-formyl complexes which may be important intermediates in the initiation step of CO reduction. We have also studied the hydrogenation of metal-carbene complexes,[3] a reaction which may be related to the chain termination step in CO reduction. Here we report (a) the Cannizzaro-like disproportionation of the neutral formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**1**)[1] to give the dimeric metallo ester $(C_5H_5)(CO)(NO)ReCH_2OC(O)Re(CO)(NO)(C_5H_5)$ (**2**) and (b) the indirect hydrolysis of this ester to give the first stable authentic hydroxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**) (Scheme I). Hydroxymethyl-metal complexes have been considered as intermediates in CO reduction but have previously been unavailable for study.[5-7]

Ester **2** was discovered during our attempts to understand the unusual behavior of $(C_5H_5)Re(CO)(NO)(CHO)$. This neutral formyl complex is only moderately air sensitive and is relatively stable in solution under nitrogen, decomposing over several days to give $(C_5H_5)Re(CO)(NO)(H)$ (**4**) as the pri-

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