

the bonds adjacent to the interage bond; MM2 predicts 1.550 Å for all six of these bonds in cubylcubane, whereas they are observed to be 1.568 (9) Å, slightly longer than the other cube edges. A much larger difference exists between the prediction, 1.551 Å, and the observation, 1.606 (6) Å, for the cube edge between the interage link and the *tert*-butyl substituent in 2-*tert*-butylcubylcubane. The origin of these differences is not clear; MM2 may treat the nonbonded interactions too softly and/or crystal packing forces may be responsible.

Supplementary Material Available: Data collection parameters and tables of atomic positional parameters, Cartesian coordinates, bond distances, bond angles, torsion angles, and anisotropic thermal parameters for cubylcubane and *tert*-butylcubylcubane (7 pages); table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

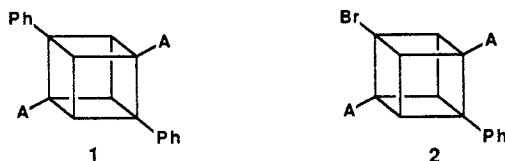
New Developments in Cubane Chemistry: Phenylcubanes

A. Bashir-Hashemi

Geo-Centers, Inc., at ARDEC
Dover, New Jersey 07806[†]

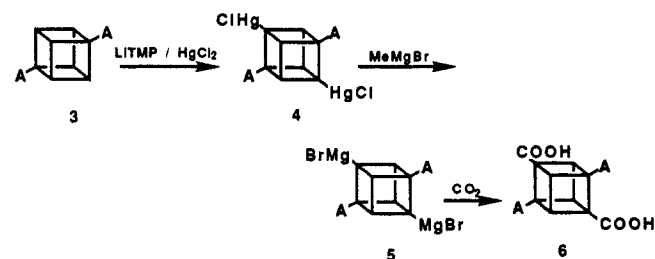
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As part of a program of research directed toward developing novel energetic materials, we have prepared diphenylcubane diamide **1** and bromophenylcubane diamide **2**.



A = C(O)N[CH(CH₃)₂]₂

Since the first synthesis of cubane,¹ there has been a great deal of effort to functionalize the cubane skeleton. Eaton et al. have recently developed a methodology in which amido cubanes can be functionalized through a reverse transmetalation procedure.² For example, the reaction of cubane diamide **3** with an excess of

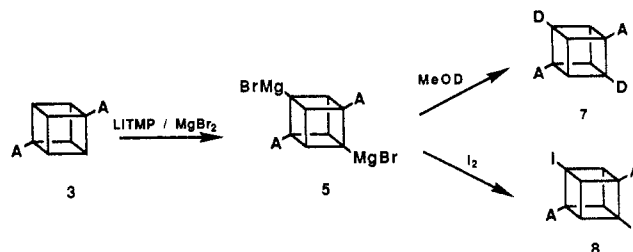


lithium tetramethylpiperidide (LiTMP) and mercuric chloride gives compound **4**, which upon reverse transmetalation with CH₃MgBr, followed by carboxylation of intermediate **5**, furnishes diacid cubane diamide **6** in a reasonable yield.

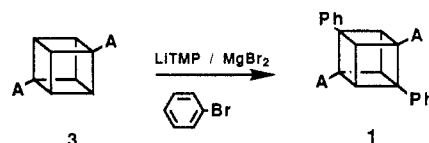
However, because of the high toxicity of organomercury compounds, scale-up of this method was limited. Therefore, it was desirable to undertake an alternate procedure in which the use

of mercury compounds would be avoided. We now report the direct and successful synthesis of **5** and its application to the synthesis of phenylcubanes.

In our hands, the reaction of cubane diamide **3** with an excess of LiTMP/MgBr₂ in THF at 0 °C, followed by quenching the reaction mixture with CH₃OD or I₂ gave dideuterated cubane diamide **7** and diiodocubane diamide **8** in 80% and 72% yields, respectively.



Perhaps the greatest significance of this procedure is that it presents a potential route for the synthesis of phenylcubanes. The synthesis of phenylcubanes has been the target of intensive studies over the last 30 years.³ To the best of our knowledge, no conclusive evidence for introducing a phenyl group to the cubane skeleton has yet been reported. In our initial attempts, cross-coupling reactions of **4** with bromobenzene⁴ or reaction of **8** with phenylboric acid⁵ using palladium catalysts were not successful. However, the reaction of cubane diamide **3** with 10 equiv of LiTMP and 4.0 equivalents of MgBr₂ etherate in THF at 0 °C, followed by the addition of 10.0 equiv of bromobenzene, gave diphenylcubane diamide **1** in 53% yield.



The structure of **1** was clear from its ¹H NMR and mass spectra.⁶ The 300 MHz ¹H NMR spectrum had six resonances at δ 0.60 (d, *J* = 6 Hz, 12 H), 1.28 (d, *J* = 6 Hz, 12 H), 3.06 and 3.20 (septets, *J* = 6 Hz, 2 H each), 4.45 (s, 4 H), 7.20–7.40 (m, 10 H). The EI mass spectrum shows a molecular ion at 510 with fragmentations at 467, 411, 382, 283, 252 (100), 128, and 100. Carbon-13 NMR and elemental analysis data were in agreement with the structure **1**.⁷

A reasonable mechanism for the formation of **1** is presented in Scheme I. In this postulated mechanism, a benzyne intermediate was formed in situ from the reaction of excess of LiTMP with bromobenzene.⁸ Benzyne subsequently reacts with di-Grignard **5** to give intermediate **9**. When the reaction mixture was quenched with I₂, compound **10** was isolated in 25% yield.

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(4) For cross-coupling reactions of mercury compounds, see: Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer Verlag: New York, 1985.

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(6) I am indebted to Dr. T.-H. Chen, ARDEC, for the mass spectra and to Dr. T. Axenrod, CCNY, for the NMR spectra.

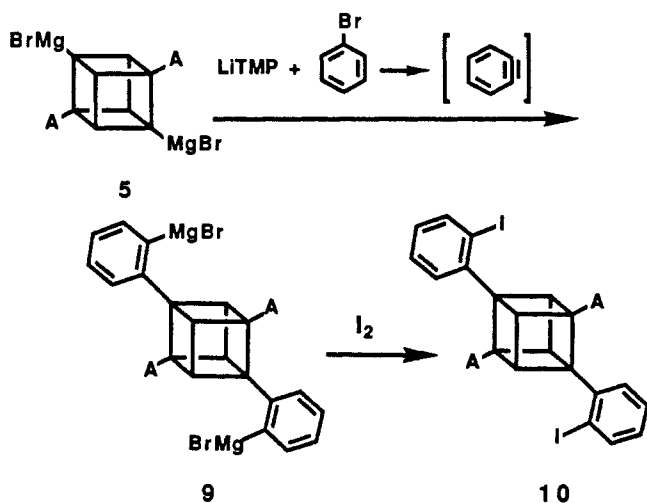
(7) The X-ray structure of the reduction product of **1**, 1,4-bis(*N,N*-diisopropylaminomethylene)-2,7-diphenylcubane, shows an unusually short bond length of 1.484 Å for the phenyl-cubane C–C bond. Details of the X-ray structure will be published elsewhere.

(8) For the chemistry of benzyne, see: Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.

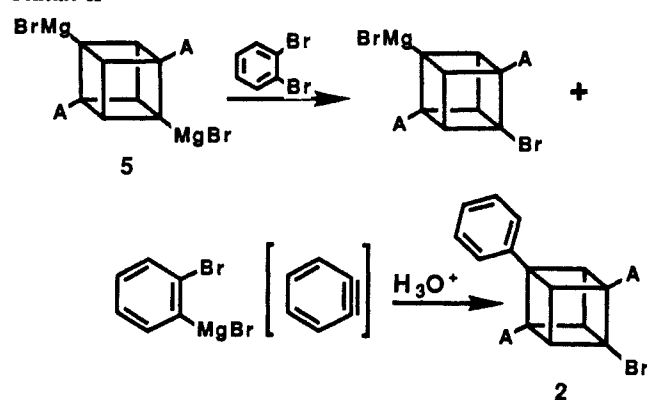
[†] Mailing address: Geo-Centers, Inc., 762 Route 15 South, Lake Hopatcong, NJ 07849

(1) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157.
(2) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 948. Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055.

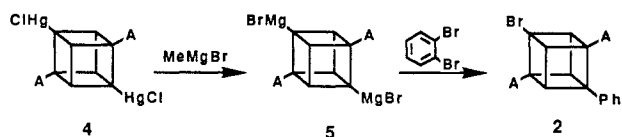
Scheme I



Scheme II



In a similar reaction cubane diGrignard 5 was prepared in situ from the reaction of cubane diamide dimercury chloride 4 and MeMgBr in THF at room temperature. Addition of dibromobenzene to this reaction mixture gave a 30% yield of bromophenylcubane diamide 2, the first cubane derivative containing three different substituents. Here, it would appear that a benzyne



intermediate formed through metal halogen exchange subsequently reacts with the second Grignard function of the cubane to give 2⁹ (Scheme II).

We are now investigating the chemistry of phenylcubanes. The results of this investigation will be published in due course.

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Registry No. 1, 116531-75-0; 2, 116531-76-1; 3, 94161-36-1; 4, 116531-77-2; 7, 116564-45-5; 8, 94138-19-9; 10, 116531-78-3; LiTMP, 38227-87-1; MgBr₂, 7789-48-2; CH₃OD, 1455-13-6; MeMgBr, 75-16-1; MgBr₂·etherate, 29858-07-9; o-dibromobenzene, 583-53-9; bromobenzene, 108-86-1.

(9) For a similar proposed mechanism, see: Du, C.-J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162. Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524.

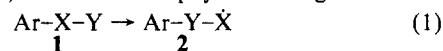
Oxidative Ring Expansion of 1-(*tert*-Butylamino)indolines to 1,4-Dihydrocinnolines. Novel Neophyl Rearrangement of Hydrazyl Radicals

S. F. Wang,[†] L. Mathew, and J. Warkentin*

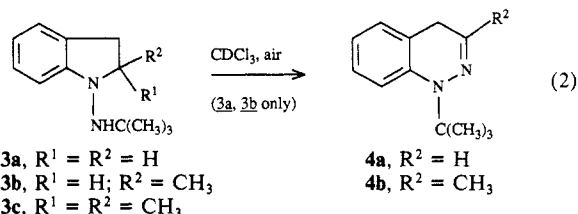
Department of Chemistry, McMaster University
Hamilton, Ontario L8S 4M1, Canada

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Free-radical rearrangements that convert one 2-aryl radical (1) to another (2) (eq 1) are called "neophyl" rearrangements and



have received much attention.¹ Examples in which X and Y of 1 are both carbon-centered are common and include the parent system (Ar = C₆H₅, X = C(CH₃)₂, Y = CH₂) that gives the class of rearrangements its name.¹ Examples of non-carbon moieties (X and/or Y of 1) are less common but include the cases X = O, Y = C-centered³ and X = C-centered, Y = O.⁴ There are still no examples, apparently, of aryl migration from C to N or from N to C,⁵ nor are rearrangements known in which both X and Y are unsaturated sites, as in 2-arylvinyll⁶ or in aryldiazonyl radicals.⁷ Other examples of eq 1 in which both X and Y are heteroatoms or heteroatom-centered, as in peroxy, aminoxy, oxaminy, and hydrazyl, appear to be unknown also. We were therefore surprised to find the clean oxidative rearrangements of 1-aminoindolines (3) to 1,4-dihydrocinnolines (4) that appear to require neophyl rearrangement of hydrazyls as a key step, eq 2.



Compounds 3 were synthesized from azo precursors (5)⁸ by free-radical chemistry reported previously,⁹ Scheme I, and they were separated from the other cyclic coproducts 6 by careful chromatography on silica gel under N₂.

Degassed solutions of 3a-c in CDCl₃, in sealed NMR tubes, were stable indefinitely at room temperature. However, when the tubes were opened and capped with plastic caps, 3a and 3b disappeared in 2-3 days with clean formation of 4a and 4b, respectively. The fact that air starts the reaction and that the products are oxidized as well as structurally rearranged, with respect to starting materials, suggests a free-radical mechanism, Scheme II. Oxidation of 3 to hydrazyl 7, followed by neophyl rearrangement¹ through diaziridine intermediate (8) to isomeric

[†]Visiting scholar from Xian Modern Chemistry Research Institute, 1986-1988.

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