the bonds adjacent to the intercage 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 intercage 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

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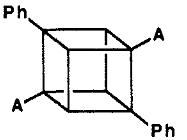
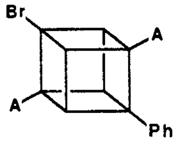
Received June 7, 1988

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



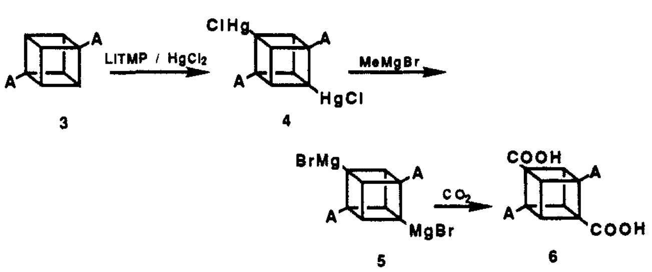
1



2

A = C(O)N[CH(CH$_3$)$_2$]$_2$

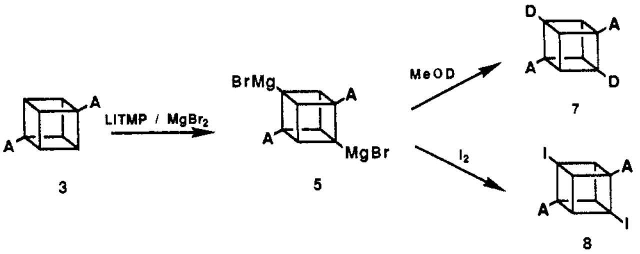
Since the first synthesis of cubane,[1] there has been a great deal of effort to functionalize the cubane skeleton. Eaton et al. have recently developed a methodology in which amido cubanes can be functionalized through a reverse transmetalation procedure.[2] For example, the reaction of cubane diamide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



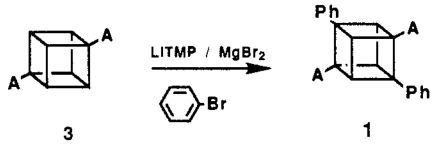
lithium tetramethylpiperidide (LiTMP) and mercuric chloride gives compound 4, which upon reverse transmetalation with CH$_3$MgBr, followed by carboxylation of intermediate 5, furnishes diacid cubane diamide 6 in a reasonable yield.

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/MgBr$_2$ in THF at 0 °C, followed by quenching the reaction mixture with CH$_3$OD or I$_2$ gave dideuteriated 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 bromobenzene[4] or reaction of 8 with phenylboric acid[5] using palladium catalysts were not successful. However, the reaction of cubane diamide 3 with 10 equiv of LiTMP and 4.0 equivalents of MgBr$_2$·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 ^{1}H NMR and mass spectra.[6] The 300 MHz ^{1}H 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 I$_2$, 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.

(5) For palladium-catalyzed cross-coupling of arylboronic acids with aryl halides, see: Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237. Sharp, M. J.; Snieckus, V. *Tetrahedron Lett.* **1985**, *26*, 5997.

(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.

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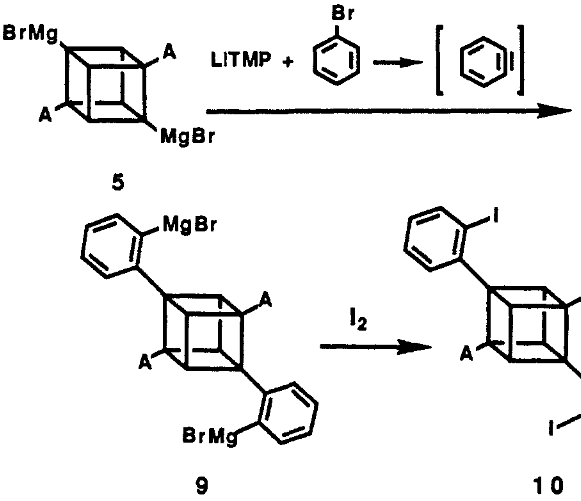
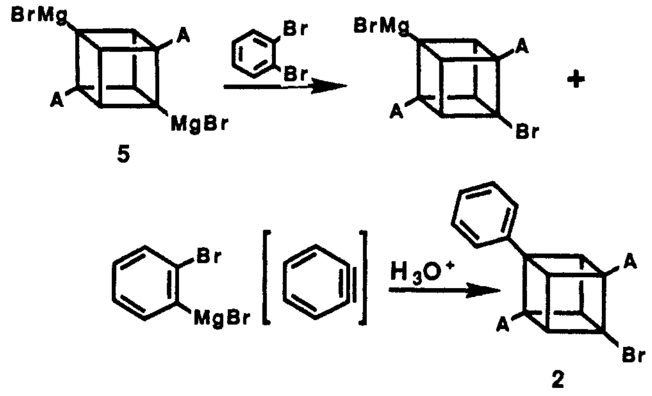
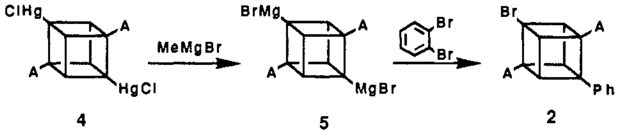
Scheme I



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 **2**[9] (Scheme II).



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

Acknowledgment. Special thanks to Professor P. E. Eaton and to Professor H. Hart for their helpful suggestions. Useful discussions with Dr. G. Doyle and Dr. D. Stec are gratefully acknowledged as well as financial support by ARDEC under contract DAAA21-86-C-0101.

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; MgBr$_2$, 7789-48-2; CH$_3$OD, 1455-13-6; MeMgBr, 75-16-1; MgBr$_2$-etherate, 29858-07-9; *o*-dibromobenzene, 583-53-9; bromobenzene, 108-86-1.

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[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

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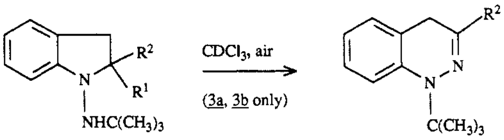
Free-radical rearrangements that convert one 2-aryl radical (**1**) to another (**2**) (eq 1) are called "neophyl" rearrangements and

$$\underset{\mathbf{1}}{\text{Ar–X–Y}} \rightarrow \underset{\mathbf{2}}{\text{Ar–Y–}\dot{\text{X}}} \qquad (1)$$

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 = C$_6$H$_5$, X = C(CH$_3$)$_2$, Y = CH$_2\cdot$) 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-centered[3] 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-arylvinyl[6] or in aryldiazenyl radicals.[7] Other examples of eq 1 in which both X and Y are heteroatoms or heteroatom-centered, as in peroxyls, aminoxyls, oxaminyls, and hydrazyls, 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.



(2)

3a, R^1 = R^2 = H
3b, R^1 = H; R^2 = CH$_3$
3c, R^1 = R^2 = CH$_3$

4a, R^2 = H
4b, R^2 = CH$_3$

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 N$_2$.

Degassed solutions of **3a–c** in CDCl$_3$, 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 rearrangement[1] through diaziridine intermediate (**8**) to isomeric

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

[1] For reviews of radical rearrangements, see: (a) Surzur, J. M. In *Reactive Intermediates*; Abrammovitch, R. A., Ed.; Plenum Press: New York, 1982; pp 121–295. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100. (c) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 161–310.

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[7] Porter, N. A.; Green, J. G. *Tetrahedron Lett.* **1975**, 2667.

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