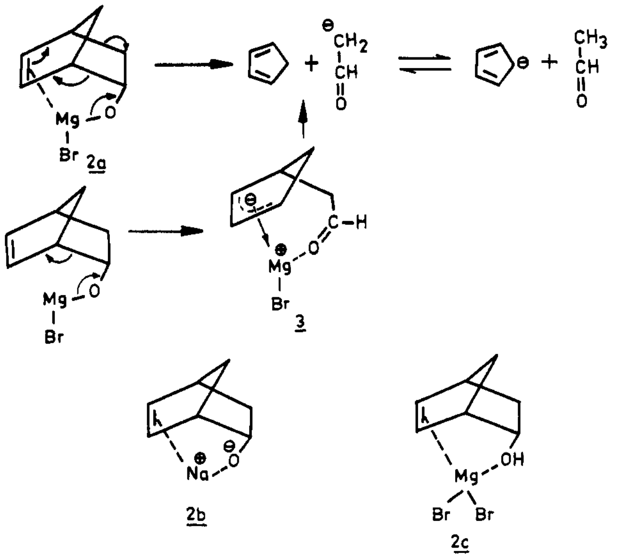
Scheme I



demonstrates the requirement of intramolecular participation by magnesium ion. The reaction need not necessarily be a concerted retro-Diels–Alder cleavage but may involve a Mg^{2+}-stabilized cyclopentenyl anion intermediate (**3**). The stability of the allylcyclopentenyl anion formed by the action of sodium on 5-(chloromethyl)norbornene and other cyclopentenyl anions has been demonstrated.[2] However, in these cases the anions do not undergo further fragmentation. In the present study no product arising from the intermediate **3** could be detected, suggesting that such an intermediate, if formed, is extremely short-lived. Hence the reaction can be formally considered to be a retro-Diels–Alder cleavage involving intermediates of type **2a**, **2b**, or **2c** either in a concerted manner or through a short-lived intermediate similar to **3**.

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(2) (a) Bates, R. B.; McCombs *Tetrahedron Lett.* **1969**, 977–8. (b) Freeman, P. K.; George, D. E.; Rao, V. N. M. *J. Org. Chem.* **1964**, *29*, 1682. (c) Freeman, P. K.; Rao, V. N. M.; George, D. E.; Fenwick, G. L. *Ibid.* **1967**, *32*, 3958. (d) Hill, E. A.; Theissen, R. J.; Doughty, A.; Miller, R. *Ibid.* **1969**, *34*, 3681.

Registry No. Ia, 694-97-3; Ia·Na, 80641-17-4; Ib, 2890-98-4; II, 542-92-7; II maleic anhydride adduct, 826-62-0; III, 75-07-0; III hydrazone, 1019-57-4; 1-phenylethanol, 98-85-1; cyclopentadiene dimer, 7313-32-8; cinnamaldehyde, 104-55-2.

J. V. N. Vara Prasad, Padmini Iyer, C. N. Pillai*
Department of Chemistry
Indian Institute of Technology
Madras 600 036, India

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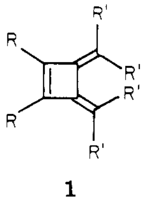
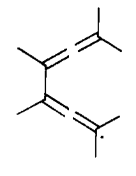
Synthesis of 3,4-Bis(alkylidene)cyclobutenes by the Reductive Dimerization of Propargyl Chlorides

Summary: The treatment of propargyl chlorides with tetrakis(triphenylphosphine)nickel(0) in benzene or tetrahydrofuran solution at 0–25 °C produces the highly reactive 3,4-bis(alkylidene)cyclobutenes in 65–75% yields.

Sir: 3,4-Bis(alkylidene)cyclobutenes (**1**) have received considerable attention from both theorists and experimentalists. Particular interest has been focused on the electronic properties of **1** relative to the isomeric benzenoid aromatics,[1,2] the thermal isomerization to isomeric structures,[3] the thermodynamic stabilities,[4] and the potential for possessing biradical properties in the ground state.[5] Typical of such interesting systems is the lack of simple methods for their synthesis. 3,4-Dimethylenecyclobutene (**1**, R = R′ = H) has been prepared via multistep pathways[6,7] which are not adaptable to the synthesis of substituted **1**′s. 1,5-Hexadiynes have been converted to **1** in a flow reactor at 335–410 °C at low pressure;[8] a procedure not readily adaptable for large-scale preparations or high-molecular-weight compounds. The thermal ring closure of 1,2,4,5-tetraenes (bisallenes, **2**) also produces **1**;[9] however, no convenient general procedure is available for the synthesis of such tetraenes. In studies in our laboratories on the mechanism of the transition metal (Fe, Co, Ni, and Cu) catalyzed formation of allenes from propargyl chlorides and Grignard reagents[10] we have discovered an exceptionally facile and general procedure for the synthesis of substituted 3,4-bis(alkylidene)cyclobutenes.

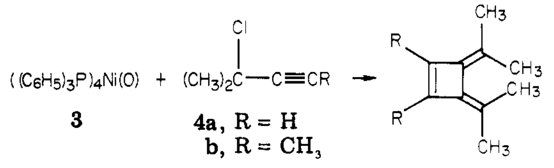


1



2

The reaction of tetrakis(triphenylphosphine)nickel(0) (**3**) with **4a** and **4b** in benzene or tetrahydrofuran at 0 °C results in the rapid formation of **5a** and **5b**. The product and solvent were removed from the inorganic residue by trap-to-trap distillation on a vacuum line. Analysis of the residue by NMR showed no characterizable organic material remaining. The dimeric nature of **5a** and **5b** was demonstrated by GC/MS (parent ion *m/e* of 134 and 162, respectively), while the presence of three double bonds was demonstrated by the absorption on 3 molar equiv of hydrogen[11] (over a 10% palladium-on-charcoal catalyst). The structures of **5a** and **5b** were readily assigned on the basis of their ^1H and ^{13}C NMR spectra.[12]



$((C_6H_5)_3P)_4Ni(0) + (CH_3)_2CCl{-}C{\equiv}CR \rightarrow$

3 **4a**, R = H
b, R = CH_3

5a, R = H
b, R = CH_3

The reaction of 3-chloro-1-butyne with **3** produces a 1:1 mixture of two dimeric products assigned structures **6** and

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(1) Heilbronner, E.; Gleiter, R.; Hopf, H.; Hornung, V.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 783.

(2) Rancurel, P.; Huron, B.; Praud, L.; Malrieu, J. P.; Berthier, G. *J. Mol. Spectrosc.* **1976**, *60*, 259.

(3) Henry, T. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 5103.

(4) Gutman, I.; Bosanac, S. *Tetrahedron* **1977**, *33*, 1809.

(5) Dohnert, D.; Koutecky, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789.

(6) Blomquist, A. J.; Maitlis, P. M. *Proc. Chem. Soc.* **1961**, 332.

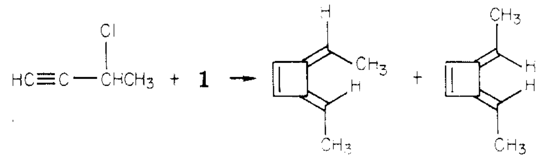
(7) Marlin, H.-D.; Kagabu, S.; Scheivek, H.-J., *Tetrahedron Lett.* **1975**, 3311.

(8) Huntsman, W. D.; Wristers, H. J. *J. Am. Chem. Soc.* **1967**, *89*, 342.

(9) Skattebol, L.; Solomon, S. *J. Am. Chem. Soc.* **1965**, *87*, 4506.

(10) Pasto. D. J.; Chou, S.-K.; Waterhouse, A.; Shults, R. H.; Hennion, G. F. *J. Org. Chem.* **1978**, *43*, 1385.

(11) The hydrogenation product from **5a** is assigned the structure *cis*-1,2-diisopropylcyclobutane: ^1H NMR ($CDCl_3$) δ 0.83 (d, J = 5.7 Hz, 12 H), 1.45–1.85 (br m, 8 H); mass spectrum parent ion calcd. for $C_{10}H_{20}$ *m/e* 140.157, observed *m/e* 140.158.



7 on the basis of their NMR spectra.[13]

The following is a typical procedure for the reductive cyclodimerization reaction. Bis(triphenylphosphine)nickel(II) dibromide (5 mmol) and triphenylphosphine (10 mmol) are dissolved in 50 mL of tetrahydrofuran at 25 °C under an argon atmosphere. Powdered zinc (50) mmol) is added and the reaction mixture is stirred at 25 °C for 30 min. The deep-red solution is cooled to 0 °C and 25 mmol of the propargyl chloride is added. (It is to be noted that the reaction is catalytic in 3 in the presence of excess zinc, although the reaction decreases in reactivity with further extent of the reaction.) After 10 min, 400 mL of pentane is added. The organic layer is decanted and is washed with ice water and is then dried ($MgSO_4$). The pentane is removed by distillation and the product is purified by trap-to-trap distillation on a vacuum line, giving 65–75% yields of product. All manipulations must be carried out under an argon atmosphere in order to avoid polymerization of the product.[8]

The mechanism of this very interesting reductive cyclodimerization is currently being investigated in our laboratories.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research (PRF No. 11713-AC1,3).

Registry No. 3, 15133-82-1; **4a**, 1111-97-3; **4b**, 999-79-1; **5a**, 3642-14-6; **5b**, 80865-52-7; **6**, 80865-53-8; **7**, 80865-54-9; 3-chloro-1-butyne, 21020-24-6; *cis*-1,2-diisopropylcyclobutane, 80865-55-0.

Daniel J. Pasto,* Dilip K. Mitra
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

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[12] **5a**: ^{1}H NMR (C_6D_6) δ 1.76 (s, 6 H), 1.93 (s, 6 H), 6.84 (s, 2 H); ^{13}C NMR (C_6D_6, proton decoupled) δ 18.6, 19.6, 111.3, 136.0; ^{13}C NMR (C_6D_6, proton nondecoupled) δ 18.6 (q of q, J = 125, 4.5 Hz, inner CH_3's, 19.6 (q of q, J = 125, 4.5 Hz, outer CH_3's), 111.3 (s, isopropylidene C), 136.0 (s, C_3 and C_4 of ring), 136.0 (d, J = 173 Hz, C_1 and C_2 of ring); mass spectrum, parent ion calcd for $C_{10}H_{14}$ m/e 134.110, observed m/e 134.111. **5b**: ^{1}H NMR (C_6D_6) δ 1.85 (s, 6 H), 1.91 (s, 6 H), 1.96 (s, 6 H); GC/MS parent ion m/e 162.

[13] NMR spectrum of the volatile fraction. **6**: (C_6D_6) δ 1.61 (d), 1.77 (d), 5.01 (q), 5.32 (q), 6.56 (s), 6.72 (s); **7**: δ 1.79 (d), 5.02 (q), 6.74 (s).

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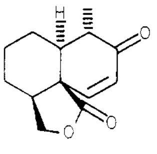
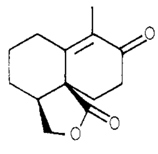
tert-Butyllithium Additions to Enones. Preferential Axial Attack

Summary: The conjugate addition of *tert*-butyllithium to cyclic enones has been shown to occur preferentially in an axial fashion.



1



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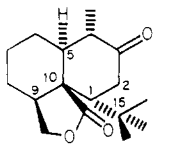

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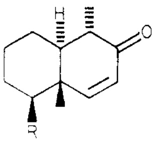
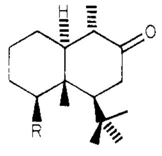
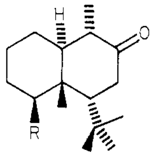


4, R = OMe
5, R = H



6, R = OMe
8, R = H



7, R = OMe
9, R = H

Sir: Six-membered rings bearing *axial tert*-butyl groups are rare. In most cases compounds which have a *tert*-butyl substituent adopt a conformation in which the bulky group is equatorial. This tendency for the *tert*-butyl group to anchor a particular chair conformation has been exploited often in studies of cyclohexane chemistry.[1]

Recently, however, a number of axial *tert*-butyl-substituted compounds have been reported.[2–6] For most of these substances the axial disposition of the bulky group results from the interplay and balance of various conformational interactions in which a particular conformer having an axial *tert*-butyl group either dominates or substantially contributes to the conformational equilbrium in solution.[2,3] For some examples an axial *tert*-butyl conformer has been shown to exist in the solid state but not necessarily in solution.[4–6] In only one case, that of 8β-*tert*-butyl-*trans*-decahydroquinoline,[7] is the *tert*-butyl group constrained to be axial regardless of the conformation of the ring system. In this report we present the preparation of three new carbocyclic compounds containing *configurationally fixed axial tert-butyl groups*. Each of the compounds is produced, moreover, as the *major product of a kinetically controlled conjugate addition reaction.*

Enone lactone 1,[8] prepared from the previously described 2[9] was treated in THF solution with 1 equiv of *tert*-butyllithium at ambient temperature. A single product,[10] the saturated keto lactone 3, mp 124–125 °C, was obtained in 60% yield. The stereochemistry assigned

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[1] Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; Chapter 8.

[2] (a) Eliel, E. L.; Knoeber, M. C. *J. Am. Chem. Soc.* **1966**, *88*, 6347. (b) *Ibid.* **1968**, *90*, 3444.

[3] (a) Van de Graaf, B.; van Bekkum, H.; van Koningsveld, H.; Sinnema, A.; van Veen, A.; Wepster, B. M.; van Wijk, A. M. *Recl. Trav. Chim. Pays-Bas.* **1974**, *93*, 135. (b) Van de Graaf, B.; Baas, J. M. A.; Wepster, B. M. *Ibid.* **1978**, *97*, 268.

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[5] Johnson, F.; Zito, S. W.; Sarma, R.; McKeever, B. M. *Tetrahedron Lett.* **1978**, 753.

[6] Geneste, P.; Kamenka, J-M.; Roques, R.; DeClercq, J. P.; Germain, G. *Tetrahedron Lett.* **1981**, 949.

[7] (a) Hargrave, K. D.; Eliel, E. L. *Tetrahedron Lett.* **1979**, 1987. (b) 1-*tert*-Butyladamantane must also necessarily have an axial *tert*-butyl group as well as an equatorial one: Woodworth, C. W.; Buss, V.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1968**, 569.

[8] For 1: ^{1}H NMR ($CDCl_3$) δ 6.90 (d, J = 10 Hz, 1 H), 6.20 (d, J = 10 Hz, 1 H), 4.70 (dd, J = 9, 4 Hz, 1 H), 4.05 (d, J = 9 Hz, 1 H), 1.35–2.50 (m, 8 H), 1.15 (d, J = 7 Hz, 3 H); IR ($CHCl_3$) 1770, 1685 cm^{-1}; mp 120–121 °C. For 3: ^{1}H NMR ($CDCl_3$) δ 3.89 (dd, J = 9.5, 4.1 Hz, 1 H), 3.79 (d, J = 9.5, 1 H), 3.17 (qd, J = 13, 6.6 Hz, 1 H), 2.86 (m, 1 H), 2.71 (ddd, J = 15.1, 6.8, 1.1 Hz, 1 H), 2.53 (dd, J = 15.1, 2.4 Hz, 1 H), 2.05 (dd, J = 6.8, 2.4 Hz, 1 H), 1.98 (m, 1 H), 1.86–1.04 (m, 6 H), 1.02 (s, 9 H), 1.00 (d, J = 6.6 Hz, 3 H).

[9] (a) Goldsmith, D. J.; John, T. K.; vanMiddlesworth, F. *Synth. Commun.* **1980**, *10*, 551. (b) Enone lactone 1 was converted into 2 in 73% overall yield by the following sequence: (1) H_2, Pd, HOAc, $HClO_4$, (2) LDA, PhSeBr, (3) O_3, CH_2Cl_2 (4) Δ, Et_2NH.

[10] Satisfactory elemental analyses or precise mass measurements were obtained for all new compounds reported herein.

0022-3263/82/1947-1382$01.25/0