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Received December 6, 1976

Reactions of Alkyl Substituted Bicyclo[3.1.0]hexatriene

Sir:

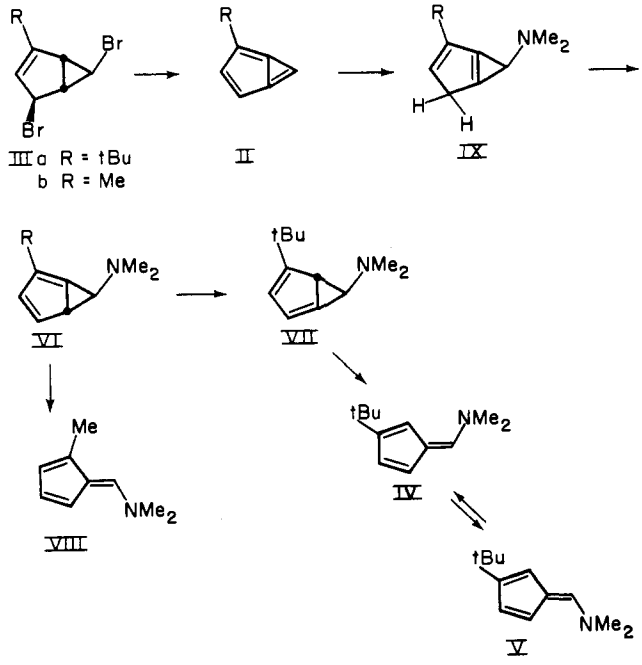
We recently reported aspects of the chemistry of bicyclo[3.1.0]hexatriene (I).[1,2] In this paper we discuss the chemical perturbation induced by substitution of an alkyl group at C_2 of I.

The precursor of 2-*tert*-butylbicyclo[3.1.0]hexatriene (IIa), 2-*tert*-butyl-4,6-dibromo-2-bicyclo[3.1.0]hexene (IIIa), was prepared from 6-bromo-3-bicyclo[3.1.0]hexen-2-one by reaction with *tert*-butyllithium followed by anhydrous HBr. Treatment of IIIa with 8 equiv of potassium *tert*-butoxide in 5 mL of THF at −70 °C for 15 h produced only one of the four possible *tert*-butyl-6-*tert*-butoxyfulvenes as judged by both ^1H NMR and ^{13}C NMR analysis.[3] Similarly, upon treatment of IIIa with 6 equiv of potassium *tert*-butoxide and 8 equiv of $HNMe_2$ in 5 mL of THF at −70 °C, a mixture of two *tert*-butyl-6-dimethylaminofulvenes, A and B, was obtained in a ratio of 3:1, respectively. This mixture of aminofulvene isomers slowly epimerized under the reaction conditions to yield a 1:1 mixture of both isomers.

These results suggest that only isomer A was initially formed as indicated by the formation of only one 6-*tert*-butoxy-*tert*-butylfulvene. From ^1H NMR of the 3:1 mixture of A:B, we knew which set of olefinic protons correlated with the initially formed isomer A and which arose from the epimer B.[4] The location of the *tert*-butyl group was established by treating the mixture of A and B with phenyllithium to form the 6-phenylfulvene followed by dimethyl acetylenedicarboxylate. The ^1H NMR of the Diels-Alder adduct, obtained in 70% overall yield, clearly indicated that the *tert*-butyl group was only present at C_2 (IV) and C_3 (V) of the original aminofulvene.[5]

However, it was not known whether structure IV or V corresponded to the initially formed isomer A. Exposure of a 1:1 mixture of A and B to a 3:1 mixture of $MeOD/CDCl_3$ at 42 °C resulted in the incorporation of 1.7 D over a 1.5-h period. By analogy to 6-dimethylaminofulvene,[6] the hydrogens at C_1 and C_4 were more easily exchanged. After deuteration, compound A possessed a singlet (1 H) at δ 6.39 ($CDCl_3$) and compound B possessed a singlet (1 H) at δ 6.62 ($CDCl_3$).

In the unsubstituted 6-dimethylaminofulvene, H_3 is upfield from H_2 by 0.20 ppm. CNDO/2 calculations predict the total electron densities on H_3 and H_2 of IV and V, respectively, to be equally perturbed by addition of a *tert*-butyl group to C_2 or C_3 of the parent compound. The anisotropic effect of the *tert*-butyl group exerted upon H_3 and H_2 should be the same for both IV and V. Therefore H_3 of IV should be upfield from H_2 of V by the same parts per million as H_3 is from H_2 for the parent aminofulvene. The correlation between the predicted



and actual spectral absorption is very good (0.20 ppm vs. 0.23 ppm). By this analysis, the initially formed isomer A corresponds to structure IV and B to structure V.

When IIIa was treated as described above except for the presence of 15 equiv of $DNMe_2$, 0.6 D was incorporated at C_6 in the product aminofulvene. On the other hand, when the 4,6-dibromobicyclo[3.1.0]hexene was treated under similar conditions, only 0.2 D was incorporated.[2] This may indicate that the lifetime of 2-*tert*-butylbicyclo[3.1.0]hexatriene, IIa, is somewhat longer than that of unsubstituted bicyclo[3.1.0]-hexatriene, thereby allowing IIa more time to exchange.

In view of the chemistry of bicyclo[3.1.0]hexatriene, the nucleophilic addition of $HNMe_2$ should entail protonation either at C_2 or C_4 of IIa. Proton delivery to C_2 of IIa should be disfavored for the same reason that protonation at the tertiary carbon of methylcyclopentadienyl anion does not occur.[7] A mechanism consistent with that elucidated for bicyclo[3.1.0]-hexatriene entails an initial trans nucleophilic addition of dimethylamine to IIa with protonation occurring at the unsubstituted C_4. A subsequent [1,5] sigmatropic shift of the hydrogen syn to the nitrogen generates the less strained diene VIa.[9] At this point, the diene VIa, instead of undergoing a disrotatory electrocyclic opening to yield the sterically conjested 4-*tert*-butyl-6-dimethylaminofulvene (VIIIa),[10] is converted to the isomeric diene VII via a base catalyzed [1,5] sigmatropic shift. VII then undergoes a ring opening to form the comparatively stable IV.

By this analysis a less bulky alkyl at C_2 of I should lead to the formation of the 4-substituted aminofulvene since the counterpart of diene VI should open directly. To test this prediction, 2-methyl-4,6-dibromobicyclo[3.1.0]hex-2-ene (IIIb) was subjected to the standard conditions. The predominant product was 6-bromo-4-methylenebicyclo[3.1.0] hex-2-ene. However, a single methyl-6-dimethylaminofulvene (C) was obtained as a minor product. Unlike the *tert*-butylfulvene IV, fulvene C did not epimerize upon purification via column chromatography.

To confirm the structure of C, methylcyclopentadienyl anion was converted to a mixture of three methyl-6-dimethylaminofulvenes using a procedure devised by Hafner.[12] By ^1H NMR and ^{13}C NMR the product, after purification by column chromatography, consisted of a 2:1:1 mixture. The major component was assigned as 4-methyl-6-dimethylaminofulvene (VIII) since under these equilibrating conditions, equal amounts of 2- and 3-methyl-6-dimethylaminofulvenes IVb and Vb should be present.[13] By ^1H NMR and ^{13}C NMR, product C corresponds to structure VIII. Just as was observed for the unsubstituted case, the disrotary opening of VI is fast compared to further [1,5] hydrogen shifts provided that the alkyl group at C_2 does not sterically interfere with ring opening.

In view of the increased rate of exchange at C_6, sterically demanding substituents may provide a means of sufficiently stabilizing I to permit observation of chemistry other than nucleophilic attack. We are presently pursuing this line of investigation.

Acknowledgment. We thank Research Corporation for financial support.

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(3) ^1H NMR ($CDCl_3$) δ 1.21 (s, 9 H), 1.41 (s, 9 H), 6.01–6.58 (m, 3 H), 7.11 (s, 1 H, H_6); ^{13}C NMR ($CDCl_3$, proton decoupled) ppm from Me_4Si 28.08 (CMe_3), 30.06 ($OCMe_3$ methyl), 107.85, 123.86, 126.54 (tertiary ring carbon), 114.15, 116.97 (quaternary ring carbon), 147.51(C_6).
(4) ^1H NMR ($CDCl_3$) δ, isomer A 1.28 (s, 9 H), 3.24 (s, 6 H), 6.39 (m, 3 H), 7.00 (s, 1 H, H_6); isomer B 1.28 (s, 9 H), 3.24 (s, 6 H), 6.15 (m, 1 H), 6.62 (m, 2 H), 7.05 (s, 1 H, H_6); ^{13}C NMR ($CDCl_3$, proton decoupled) ppm from Me_4Si, 1:1 A and B 31.20 (CMe_3), 43.11 (NMe_2), 107.00, 114.73, 117.14, 119.28, 125.04, 125.32 (tertiary ring carbons), 147.00, 147.17 (C_6); mass spectrum mixture A and B (*m/e*) parent 177 (%RA = 29), 162 (%RA = 100).
(5) ^1H NMR ($CDCl_3$) δ, mixture of two isomers, 1.10 (s, 9 H), 3.84 (s, 6 H), 4.27 (m, 1 H), 4.77 (m, 1 H), 5.38 (m, 1 H), 6.50 (m, 1 H), 7.27 (m, 5 H); mass spectrum (*m/e*) parent 352 (%RA = 86), 292 (%RA = 100).
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(9) The implicit assumption is that the rearrangement of II to VI proceeds with the same selectivity with respect to hydrogen migration as did the analogous transformation of the unsubstituted bicyclo[3.1.0]hexatriene.[1,2] Consequently, only the hydrogen syn to the heteroatom at C_6 of IXa should undergo a [1,5] sigmatropic migration. Additional support for this mechanism is provided by the exclusive formation of IV as the initial product. If both the syn and anti methylene hydrogens of IXa were equally prone to migration, both IV and V would have been produced. Compound VI and VII cannot be in equilibrium with each other in order for the results to be consistent with those obtained from the analogous deuterium labeled compounds.
(10) One measure of the steric crowding induced by a *tert*-butyl group at C_1 of C_4 of 6-dimethylaminofulvene (X) is provided by the fact that alkylation of X with *t*-BuCl/$AlCl_3$ leads exclusively to the formation of 2- and 3-*tert*-butyl-6-dimethylaminofulvene. On the other hand, less hindered electrophiles exclusively attacked positions 1 and 4, the sites of highest electron density.[6,11]
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(13) 4-Methyl-6-dimethylaminofulvene: ^1H NMR (CCl_4) δ, 2.08 (s, 3 H), 3.02 (s, 6 H), 5.70–6.37 (m, 3 H), 6.65 (s, 1 H, H_6); ^{13}C NMR ($CDCl_3$, proton decoupled) ppm from Me_4Si 15.16 (CH_3), 42.52 (NMe_2), 111.04, 121.57, 124.93 (tertiary ring carbon), 146.18 (C_6).

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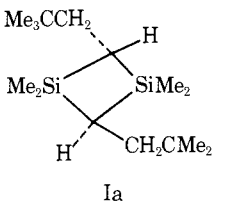
Received November 3, 1976

The Addition of *tert*-Butyllithium to Vinylhalosilanes. A Novel, High Yield Route to 1,3-Disilacyclobutanes

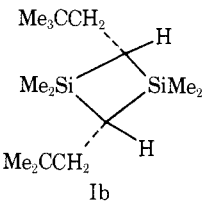
Sir:

Since the initial discovery of the addition of organolithium reagents to vinylsilanes by Cason and Brooks,[1] there have been relatively few reports of such reactions.[2] To our knowledge, the only example of the addition of an organolithium reagent to a vinylsilane bearing substituents susceptible to nucleophilic displacement on silicon is contained in the original report. Cason and Brooks observed a 4% yield of β-phenethyltriphenylsilane after hydrolytic workup of the mixture resulting from the reaction of excess phenyllithium with vinyltrichlorosilane in ether.[1] However, alkoxy and chloro groups on silicon have been found to activate vinylsilanes toward the addition of Grignard reagents.[3] We report here a novel, high yield synthesis of substituted 1,3-disilacyclobutanes, from the reaction of *tert*-butyllithium with vinyldimethylchlorosilane.

In an attempt to prepare vinyldimethyl-*tert*-butylsilane, 100 mmol of *tert*-butyllithium in 141 mL of pentane was added slowly to 100 mmol of vinyldimethylchlorosilane in 50 mL of dry hexane, under an argon atmosphere at room temperature. An exothermic reaction with the immediate formation of a white precipitate occurred. Hydrolytic workup gave, instead of the desired product, 6.55 g (46%) of I; bp 72–98 °C (1 mm); identified on the basis of data given below as a mixture of the *E* (Ia) and *Z* (Ib) isomers of 1,1,3,3-tetramethyl-2,4-di-



Ia



Ib