

for **1a**, 3.7 ppm for **1b**, 2.2 ppm for **1c**, and 1.9 ppm for **1d**. Now, since hydrocarbon **5** and heterobicyclic **1** share a common basic skeleton, we may safely attribute these residual differences chiefly, if not exclusively, to lone pair-induced enhancement of the ethylene group's  $\pi$  electron density.<sup>5</sup> We conclude, therefore, that the lone pair in **1** does partake in nonbonded interaction and, judging from the relative magnitude of the above-noted  $\Delta\Delta\delta$  terms, that the extent of such interaction increases in the order  $O \sim \text{NCN} < S < \text{NH}$ .

Continuing our analysis of the data we now make note of the fact that the chief influence that nonbonded lone pair transfer is expected to exert on the heteroatomic bridge of a molecule such as **1** is to enhance its effective electronegativity. Translated into  $^{13}\text{C}$  NMR observables, this anticipated increase in heteroatom electronegativity should manifest itself primarily as an increase in the magnitude of the  $^{13}\text{C}$ -H coupling constant of the "bridgehead" position, C(1), i.e., the carbon center directly linked to the bridge.<sup>6</sup> In fact, by following the change of this  $^{13}\text{C}$  NMR constant during the structural transition of the 9-heterononabicyclo[4.2.1] frame from saturated **4** to partially unsaturated **2**, **3** and, finally to fully unsaturated **1**, it becomes possible to gain knowledge about the mechanism of nonbonded interaction and draw inference about its dependence on the nature of the bridging unit. To begin with, one notes that the fully saturated **4** does manifest the expected dependence of  $J_{\text{C}(1)\text{-H}}$  on heteroatom electronegativity, the recorded  $\Delta J$  (**4**) differential between the two extreme cases, i.e., for  $X = \text{NH}$  and  $X = \text{O}$ , rising to an impressive 11 Hz. Similar trends are also observed with the partially saturated models **2** and **3**, the corresponding differential between extreme cases (a and d) being here 7 and 12 Hz, respectively. Turning now to the key trienic frame **1** we discover that azabicyclic **1a** fails to properly correlate with the other three members of the series due to a sharp increase in the magnitude of  $J_{\text{C}(1)\text{-H}}$  over and above that expected on the basis of values obtained from model transformations. Specifically, one finds the increase in this constant to be significantly greater (100%+) in the transformation **4a** to **1a** (11 Hz) than the combined differential (5 Hz) associated with model changes **4a**  $\rightarrow$  **2a** (3 Hz) and **4a**  $\rightarrow$  **3a** (2 Hz)! In distinct contrast to this discrepancy in  $\Delta J$  between *model* and *actual* transformation when  $X = \text{NH}$ , one finds the other members of the series, i.e., those with  $X = \text{S}$ ,  $\text{NCN}$ , and  $\text{O}$ , to be associated with virtually identical (within 1 Hz) *actual* (**4**  $\rightarrow$  **1**) and *model* (**4**  $\rightarrow$  **2** + **4**  $\rightarrow$  **3**)  $\Delta J$  differentials. Recalling now that heteroatom electronegativity in **1** must have decisive influence on the magnitude of  $J_{\text{C}(1)\text{-H}}$  (vide supra) we interpret the discrepancy in  $\Delta\Delta J$  observed between **1a** and **1(b,c,d)** to mean that when exposed to the  $\pi$  environment of **1**, the molecule's heteroatomic bridge experiences a decisive surge in electronegativity for  $X = \text{NH}$  but not for  $X = \text{S}$ ,  $\text{NCN}$ , or  $\text{O}$ . Translating this information to nonbonded interaction, one is drawn to the inevitable con-

clusion that: among the four heterotrienes examined here, only azabicyclic **1a** is endowed with what might safely be termed a bicycloconjugated frame.<sup>8</sup> The lone pair participation deduced for **1b**, **1c**, and **1d** on the basis of the "chemical shift" differential (vide supra) must thus be attributed chiefly to homoconjugative interaction<sup>9</sup> between lone pair and, judging from the direction of electron transfer, ethylene appendage.

Gratifyingly, the conclusions arrived at in the present study closely parallel those derived earlier from PES information.<sup>1-3</sup> We conclude by pointing to a striking parallel between bicycloconjugation in the 9-heterobicyclo[4.2.1]nona2,4,7-trienes and conventional conjugation in the heteronins.<sup>10</sup> In both cases heteroatomic participation is activated by the loosely held lone pair of nitrogen and inhibited by the more tightly bound counterpart of oxygen.

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- (7) As judged by the close similarity of the  $J_{\text{C}(1)\text{-H}}$  term, the electronegativity of the NH unit in **1** is seen to be nearly as pronounced as that of its normally far more demanding counterparts NCN and O!
- (8) The term bicycloconjugation is employed here to denote simultaneous interaction of the lone pair with the two formally isolated  $\pi$  appendages.
- (9) The term homoconjugation is utilized here to describe the interaction of the lone pair with only one of the two formally isolated  $\pi$  segments, irrespective of whether the process operates through bonds or through space.
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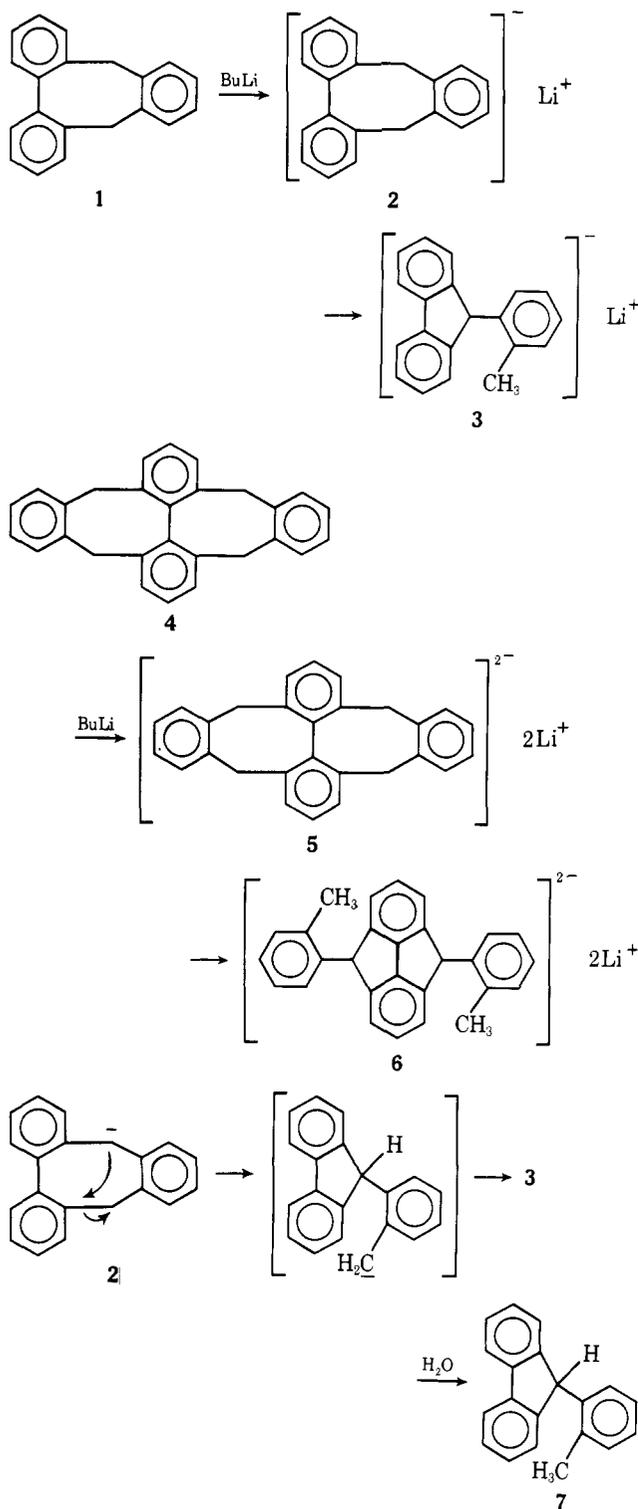
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## A Novel Base-Catalyzed Rearrangement. Formation of Dibenzo[cd,gh]pentalenide Dianion

Sir:

Molecular rearrangements are of great significance both as synthetic tools and in mechanistic studies. Most rearrangements, especially in the aromatic series, are acid-catalyzed and only a few are base-catalyzed.<sup>1</sup> A well-known base-catalyzed rearrangement in the aromatic series is the Smiles rearrangement<sup>2</sup> in which a carbanion in a system including a heteroatom is rearranged. For example, a system



with a sulfone group rearranges to a stabilized sulfonate. We wish to report a novel base-catalyzed rearrangement of hydrocarbons which initiates with the formation of a carbanion at a saturated carbon atom followed by an anionotropic process, viz., the rearrangement of tribenzo[*a,c,f*]cyclooctyl anion, **2**, to 9-(2-tolyl)fluorene anion, **3**, and of tetrabenzo[*a,de,h,kl*]bicyclo[6.6.0]tetradecyl anion, **5**, to 4,8-bis(2-tolyl)dibenzo[*cd,gh*]pentalene dianion, **6**. The latter process represents a new and easy route for obtaining the 4,8-dihydrodibenzo[*cd,gh*]pentalene system (vide supra).

2,2'-Dihydroxymethylbiphenyl<sup>3</sup> reacts with benzene in concentrated sulfuric acid at 30 °C to form tribenzocyclooctane, **1**,<sup>4,5</sup> mp 119–120 °C (colorless, cyclohexane, 70% yield), *m/e* 256 (M, 100%);  $\lambda_{\max}^{\text{C}_6\text{H}_{12}}$  237 s ( $\epsilon$  9000), 265 s (1480),

and 273 nm (1110);  $^1\text{H NMR}^6$   $\delta$  ppm (CDCl<sub>3</sub>) 3.65 (s, 4 H, benzylic), 7.18 (m, 4 H, aromatic), 7.30 (m, 8 H, aromatic). Treatment of **1** with BuLi (THF-*d*<sub>8</sub>, room temperature, 12 h) produced a red solution. Its  $^1\text{H NMR}^6$  ascribed to **2**:  $\delta$  ppm 3.10 (d, 1 H, *J* = 12 Hz), 3.87 (s, 1 H), 5.47 (d, 1 H, *J* = 12 Hz), 5.59 (t, 1 H, *J* = 7 Hz), 5.90 (m, 2 H, aromatic), 6.30 (m, 5 H, aromatic), 6.90 (m, 4 H, aromatic). Double resonance experiments have shown that the two doublets at 3.10 and 5.47 ppm are coupled. Quenching of **2** with wet ether gave **1**. Reaction of **1** with BuLi in HMPT in a NMR tube for 1 h at 80 °C revealed a new set of peaks in the NMR, followed by the disappearance of the bands of **2**. This process was completed at 120 °C. A spectrum of the aromatic moiety of the fluorene anion **3** was observed.  $^1\text{H NMR}^6$   $\delta$  ppm 6.31 (t, 2 H, *J*<sub>1</sub> = 7.0, *J*<sub>2</sub> = 7.5 Hz, H<sub>3</sub>, H<sub>6</sub>), 6.67 (t, 2 H, *J*<sub>1</sub> = 7.0, *J*<sub>2</sub> = 8.0 Hz, H<sub>2</sub>, H<sub>7</sub>), 7.08 (d, 2 H, *J* = 8.0 Hz, H<sub>1</sub>, H<sub>8</sub>), 7.76 (d, 2 H, *J* = 7.5 Hz, H<sub>4</sub>, H<sub>5</sub>).<sup>7</sup> The *o*-tolyl spectrum (4 H) appeared as follows:  $\delta$  ppm 6.59 (m), 6.85 (m), 7.14 (m), and 7.44 (d, *J* = 7.0 Hz). Quenching with wet ether resulted in a solid, mp 86 °C (ethanol, yield 70%) *m/e* 256, identified as 9-(2-tolyl)fluorene,<sup>7,4</sup> (melting point, mixture melting point,<sup>8</sup> NMR<sup>8,9</sup>). Sodium borohydride reduction of biphenyl-2,2',6,6'-tetracarboxaldehyde<sup>10</sup> afforded 80% of crude 2,2',6,6'-tetrahydroxymethylbiphenyl, *m/e* 238 (30%, M - 2H<sub>2</sub>O), 220 (40%, M - 3H<sub>2</sub>O), 206 (100%, C<sub>16</sub>H<sub>14</sub>), 202 (M - 4H<sub>2</sub>O). Its reaction with benzene in concentrated sulfuric acid (30 °C) yielded tetrabenzo[*a,de,h,kl*]bicyclo[6.6.0]tetradecane (**4**)<sup>4</sup> mp 278 °C (colorless, cyclohexane, 60% yield), *m/e* 358 (M, 100%);  $\lambda_{\max}^{\text{C}_6\text{H}_{12}}$  240 s ( $\epsilon$  9500), 265 (1800), and 273 nm (1390);  $^1\text{H NMR}^6$   $\delta$  ppm (CDCl<sub>3</sub>) 3.70 (s, 8 H, benzylic), and 7.16–7.19 (m, 14 H, aromatic). Treatment of **4** with BuLi (THF-*d*<sub>8</sub>, room temperature, 12 h) resulted in a dark red solution. Its  $^1\text{H NMR}^6$  ascribed to **5**.  $^1\text{H NMR}^6$   $\delta$  ppm 2.72 (d, 2 H, *J* = 12 Hz), 4.67 (d, 2 H, *J* = 12 Hz), 5.38 (t, 2 H, *J* = 7 Hz), 5.87 (m, 4 H, aromatic), 6.11 (m, 4 H, aromatic), 6.40 (m, 4 H, aromatic). Here too both doublets are coupled. Quenching of **5** with wet ether gave **4**. Reaction of **4** with excess BuLi in HMPT (150 °C, 1 h, inert atmosphere) revealed the following  $^1\text{H NMR}^6$  spectrum,  $\delta$  ppm 6.41 (d, *J* = 7.3 Hz), 6.68 (t, *J* = 7.3 Hz), and an aromatic multiplet 6.80–7.47 ppm. This spectrum is assigned to **6**. Quenching of **6** with wet ether produced a white solid mp 195 °C (cyclohexane, 50% yield from **4**),<sup>4</sup> *m/e* 358 (M, 100%), 266 (M - C<sub>7</sub>H<sub>7</sub>, 90%);  $\lambda_{\max}^{\text{EtOH}}$  271 ( $\epsilon$  11 800), 287 (14 700), 295 (11 100), 305 nm (3500);  $\nu_{\max}^{\text{KBr}}$  3060, 2920, 1460, 1420, 1100, 695 cm<sup>-1</sup>. A complex  $^1\text{H NMR}$  spectrum<sup>6</sup> is obtained at +31 °C due to hindered rotation and the presence of geometrical isomers.<sup>8,9</sup> The absorptions assigned to the methyl groups and the benzylic protons are broad and change upon heating and cooling:  $\delta$  (CDBr<sub>3</sub>) ppm 0.05, 1.25, 2.65, 3.70 (6 H, Me protons), 3.85, 4.80, 5.10 (2 H, benzylic protons), 6.88–7.36 (14 H, aromatic). At 180 °C the bands at 1.25 and 2.65 ppm coalesce, and the benzylic absorption appears at 4.35 and 4.50 ppm.<sup>9c</sup>

On the basis of the spectral data of the anions and the hydrocarbons obtained from the quenching of the anions, it seems that the novel carbanionic rearrangement is an easy path to dibenzo[*cd,gh*]pentalene dianion substituted in positions 4 and 8, viz., **6** as well as to 4,8-dihydro-4,8-bis(2-tolyl)dibenzo[*cd,gh*]pentalene. The NMR spectrum of **6** is very similar to that of dibenzo[*cd,gh*]pentalene dianion reported by Trost and Kinson.<sup>11</sup>

It has been pointed out<sup>11</sup> that the synthetic challenge of systems related to dibenzo[*cd,gh*]pentalene lies in their high strain energy; i.e., it is necessary to bridge a distance of 3.31 Å by a single carbon atom. The ease with which **6** is obtained reflects the energy gained by the formation of the aromatic dianion, a perturbed [12]annulenyl dianion.<sup>11</sup> The polycyclic system of dibenzo[*cd,gh*]pentalene has previously been prepared by a long and tedious route.<sup>11</sup> The rearrangement and

quenching probably proceed via the mechanism ascribed for the reaction  $2 \rightarrow 3 \rightarrow 7$ .

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## The Preservation of Metal-Carbon Bonds and Metalloid-Carbon Bonds during Direct Fluorination: a Surprise Even to Fluorine Chemists

Sir:

Occasionally chemical experiments prove successful which surprise even the researchers initiating the work. Such is the case with the preservation of metal-carbon bonds during direct fluorination.

Before the fact, one could have written general logical mechanisms for elimination of methyl groups or cleavage of all metal-carbon bonds such that certain failure would be projected. These pathways still contribute to the overall reaction even under the reported conditions but are not catastrophic.

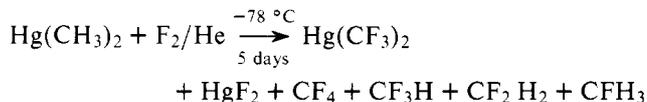
We have demonstrated preservation of mercury-carbon and silicon-carbon bonds during the process of direct fluorination by the fluorination of dimethylmercury to give bis(trifluoromethyl)mercury and of tetramethylsilane to give a series polyfluoro-tetramethylsilanes. The versatility of the method of direct fluorination has been previously demonstrated by the fluorination of structurally unusual hydrocarbons,<sup>1</sup> polymers,<sup>2</sup> and inorganic compounds<sup>3</sup> to mention just a few.

Table I<sup>a</sup>

|  | <sup>1</sup> H <sup>b</sup> |                   |                 |                  |                 | <sup>19</sup> F <sup>c</sup> |                 |                  |                 |                 |
|--|-----------------------------|-------------------|-----------------|------------------|-----------------|------------------------------|-----------------|------------------|-----------------|-----------------|
|  | CH <sub>3</sub>             | CH <sub>2</sub> F | J <sub>HF</sub> | CHF <sub>2</sub> | J <sub>HF</sub> | CH <sub>2</sub> F            | J <sub>HF</sub> | CHF <sub>2</sub> | J <sub>HF</sub> | J <sub>FF</sub> |
| Si(CH <sub>3</sub> )(CH <sub>2</sub> F) <sub>2</sub> (CHF <sub>2</sub> ) | -0.06                       | 4.32              | 47.3            | 5.68             | 45.9            | 199.60                       | 47.0            | 61.08            | 45.8            | 1.5             |
| Si(CH <sub>2</sub> F) <sub>2</sub> (CHF <sub>2</sub> ) <sub>2</sub>      |                             | 4.66              | 46.6            | 5.91             | 45.4            | 202.87                       | 46.4            | 59.88            | 45.4            | 2.0             |
| Si(CH <sub>2</sub> F) <sub>3</sub> (CHF <sub>2</sub> )                   |                             | 4.54              | 46.6            | 5.87             | 45.4            | 201.41                       | 46.6            | 60.03            | 45.4            | 1.7             |
| Si(CH <sub>2</sub> F)(CHF <sub>2</sub> ) <sub>3</sub>                    |                             | 4.68              | 46.2            | 5.82             | 45.0            | 204.39                       | 46.6            | 59.57            | 45.0            | 2.4             |
| Si(CH <sub>2</sub> F) <sub>4</sub>                                       |                             | 4.24              | 47.0            |                  |                 | 200.13                       | 46.9            |                  |                 |                 |

<sup>a</sup> All samples were run as neat liquids. Shifts are in parts per million. Coupling constants are in hertz. <sup>b</sup> + downfield from external  $\text{Me}_4\text{Si}$ . <sup>c</sup> + upfield from external TFA.

Dimethylmercury can be fluorinated to its perfluoro analogue, bis(trifluoromethyl)mercury, by low temperature fluorination. Yields of 6.5% (based on 1.53 g of  $\text{Hg}(\text{CH}_3)_2$ ) can be obtained by fluorination at  $-78$  to  $-90$  °C. A fluorine concentration of 1.67%, obtained using a mixture of 1  $\text{cm}^3/\text{min}$  fluorine to 60  $\text{cm}^3/\text{min}$  helium, was used for 5 days in the cryogenic zone reactor.<sup>1</sup> The bis(trifluoromethyl)mercury was separated from fluorocarbons and unreacted dimethylmercury on a vacuum line. The reaction can be represented as follows.



The physical properties and <sup>19</sup>F NMR agree with authentic samples prepared by alternative methods.<sup>4</sup> It has been found that  $\text{Hg}(\text{CF}_3)_2$  does not react with 3%  $\text{F}_2$  at  $-78$  °C. It has also been found that  $\text{Hg}(\text{CF}_3)_2$  does react slowly with 3% fluorine at 0 °C and appreciably at room temperature, forming  $\text{HgF}_2$  and  $\text{CF}_4$ .

We have found it possible to preserve silicon-carbon bonds under low temperature direct fluorination and are able to isolate many polyfluorotetramethylsilanes produced by controlled low temperature fluorination of tetramethylsilane. Using 1.67% fluorine, obtained by combining flows of 1  $\text{cm}^3/\text{min}$  fluorine and 60  $\text{cm}^3/\text{min}$  helium, in a cryogenic zone reactor<sup>1</sup> in which 1.65 g of tetramethylsilane has been frozen at  $-110$  °C, one can recover up to 75% of the fluorine substituted starting material containing all four silicon-carbon bonds intact. Varying degrees of fluorination are observed. Compounds of the type  $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$ ,  $x + y + z = 4$ , have been isolated and characterized (see Table I). Under the above conditions, we did not isolate any fluoromethylsilanes of the type  $\text{Si}(\text{CH}_3)_3\text{F}$ ,  $\text{Si}(\text{CH}_3)_2\text{F}_2$ , and  $\text{Si}(\text{CH}_3)\text{F}_3$ . Several of the compounds are listed below along with their proton and fluorine NMR's. A considerable degree of fluorination results under the above conditions. In fact, only at  $-150$  °C can one slow the fluorination process to allow the isolation of a single partially fluorinated species,  $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$  (55% yield), as the sole product along with unreacted tetramethylsilane. The infrared, mass spectrum, and NMR of  $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$  agree with that reported in the literature.<sup>5</sup>

Rapid metal-carbon bond vibrational and translational relaxation processes occurring at cryogenic surfaces may account for the isolation of these compounds. Obviously, the formation of three hydrogen fluoride molecules and three carbon fluorine bonds per methyl group is so exothermic that one could not explain the retention of metal-carbon bonds on energetic grounds. Work is now underway on the tungsten hexamethyl system and successful preliminary results have been achieved with a number of metal alkyl systems such as cadmium and tin.

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