

## Alkylidenecarbene Insertions into Aromatic C–H Bonds in Solution

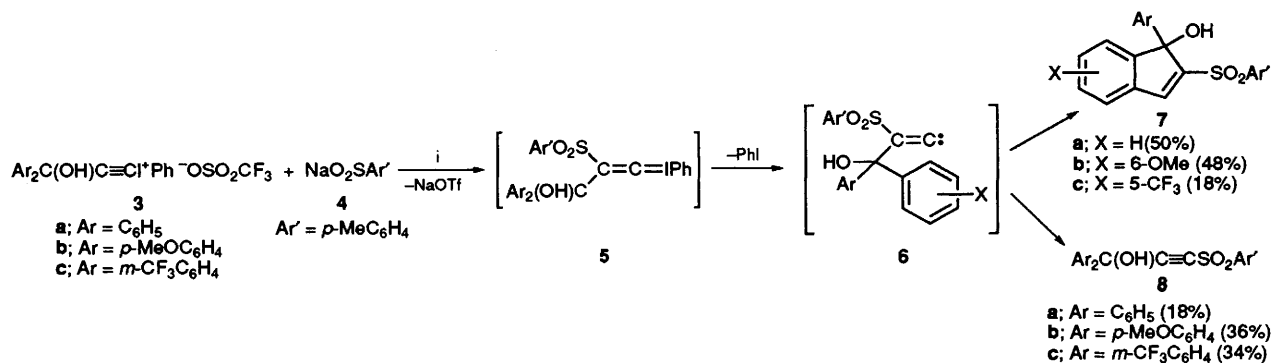
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Reaction of sodium toluene-*p*-sulfinate with  $(Ar)_2(OH)CC\equiv C(Ph)(OSO_2CF_3)$  results in substituted indenenes *via* alkylidenecarbene aromatic C–H bond insertions.

Carbenes, **1**, continue to be of considerable current research interest and activity.<sup>1</sup> The major modes of reaction of these low valent carbon intermediates are either insertions or additions.<sup>1,2</sup> Carbenes readily insert into saturated benzylic, tertiary, secondary and primary C–H bonds. Whereas inser-

tion into aromatic and vinylic C–H bonds is much less common, presumably due to the stronger bond energy of a  $C_{sp^2}$ -H bond compared with a  $C_{sp^3}$ -H bond. A similar situation exists with alkylidenecarbenes, **2**. However, these unsaturated intermediates undergo aromatic C–H insertion



Scheme 1 Reagents and conditions: i,  $CH_2Cl_2$ , 25 °C, 15 min

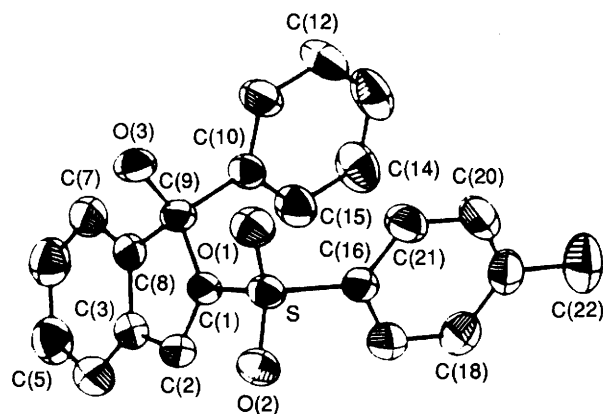


Fig. 1 X-Ray structure of 7a

only under flash vacuum pyrolysis conditions<sup>3,4</sup> (gas phase, 550–850 °C) with no such insertions known to occur in solution. Here, we report the first example of the insertion of alkylidenecarbenes into aromatic C–H bonds in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

Reaction of alkynyl(phenyl)iodonium triflates 2<sup>†</sup> with sodium toluene-*p*-sulfinate 4 affords indenenes 7 and 1-alkynyl sulfones 8 (Scheme 1). All products were completely characterized by spectral and analytical means.<sup>‡§</sup> The structure of

<sup>†</sup> Prepared<sup>5</sup> as follows: HC≡C–Li + Ar<sub>2</sub>C=O → HC≡CC(OH)Ar<sub>2</sub> → Bu<sub>3</sub>SnC≡CC(OH)Ar<sub>2</sub> → 3.

<sup>‡</sup> Iodonium salts 3a–c were filtered at –78 °C and transferred at –78 °C to CH<sub>2</sub>Cl<sub>2</sub> (50 ml) at 25 °C. NaSO<sub>2</sub>Ar' was added immediately to the stirred solution and allowed to react for 15 min. The reaction mixture was reduced *in vacuo* and filtered through a silica plug with 60 ml of diethyl ether. Radial chromatography (15% ethyl acetate–hexanes) and crystallization from CH<sub>2</sub>Cl<sub>2</sub> by the addition of hexanes gave 7a–c and 8a–c. Selected data: 7a: colourless crystals; m.p. 160–161 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.74 (s, 1 H), 7.46 (d, 1 H), 7.28 (m, 5 H), 7.1–6.9 (m, 7 H), 4.30 (s, 1 H, OH), 2.31 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.2, 149.6, 143.9, 142.4, 138.2, 136.9, 130.4, 129.2, 128.9, 128.1, 127.6, 127.1, 124.9, 124.5, 123.7, 85.5, 21.5; EI HRMS *m/z* 362.0962 M<sup>+</sup>, calc. for C<sub>22</sub>H<sub>18</sub>SO<sub>3</sub> 362.0977. 7b: white solid; m.p. 186–187 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.62 (s, 1 H), 7.32 (d, 2 H), 6.98 (m, 4 H), 6.89 (d, 2 H), 6.77 (dd, 1 H), 6.46 (d, 2 H), 4.34 (s, 1 H, OH), 3.77 (s, 3 H), 3.70 (s, 3 H), 2.30 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 160.4, 158.9, 150.8, 144.1, 143.9, 141.7, 138.3, 137.1, 130.4, 129.2, 127.7, 126.2, 124.4, 115.3, 113.5, 110.4, 84.7, 55.6, 55.1, 21.5; EI HRMS *m/z* 422.1209 M<sup>+</sup>, calc. for C<sub>24</sub>H<sub>22</sub>SO<sub>5</sub> 422.1188. 7c: colourless crystals; m.p. 176–177 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.84 (s, 1 H), 7.634 (s, 1 H), 7.631 (s, 1 H), 7.48 (d, 1 H), 7.32 (m, 3 H), 7.24 (t, 2 H), 7.00 (m, 3 H), 4.49 (s, 1 H, OH), 2.30 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.2, 151.5, 145.1, 141.2, 140.2, 138.7, 135.7, 132.3 (q), 130.7 (q), 129.6, 129.2, 128.4, 127.7, 126.9 (q), 125.0, 124.6 (q), 123.11 (q, CF<sub>3</sub>), 123.10 (q, CF<sub>3</sub>), 121.8 (q), 120.7 (q), 84.8, 21.4. Satisfactory elemental analysis was obtained.

<sup>§</sup> Spectral and analytical data for 8a–c were consistent with proposed structures and published data.<sup>6</sup>



the insertion product 7a was unambiguously assigned by X-ray determination (Fig. 1).<sup>¶</sup> Both indenenes 7 and sulfones 8 are clearly derived from the intermediate alkylidenecarbenes 6, that in turn derive from the ylide 5, the result of Michael addition of 4 to the β-carbon of the electron deficient alkyne 3.<sup>5</sup> The alkynyl sulfones are the result of the intramolecular rearrangement (migration) of carbene 6, whereas the indenenes are the consequence of a 1,5-intramolecular aromatic C–H insertion. As seen, insertion occurs in both activated and deactivated aromatic rings, albeit the deactivating CF<sub>3</sub> group considerably diminishes the yield of insertion product. Indenenes 7 provide *prima facie* evidence for alkylidenecarbene insertion into C–H bonds and represent the first example of such an insertion in solution under mild conditions.<sup>||</sup>

Financial support by the NCI of NIH (2RO1CA16903) is gratefully acknowledged.

Received, 15th July 1993; Com. 3/04148D

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<sup>¶</sup> Crystal data for 7a: S<sub>1</sub>O<sub>3</sub>C<sub>22</sub>H<sub>18</sub>; 0.45 × 0.40 × 0.15 mm, monoclinic, space group, P2<sub>1</sub>/n with *a* = 13.780(2), *b* = 6.596(1), *c* = 20.046(4) Å, β = 101.10(1)°, *V* = 1787.92 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.346 g cm<sup>-3</sup>; Mo-Kα (λ = 0.71073 Å); μ = 1.901 cm<sup>-1</sup>, 3.00 < 2θ < 48.00. X-Ray data for 7a were collected using a Syntex P1 diffractometer. The structure was solved by standard heavy-atom techniques with the SDP/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Final *R*(*R<sub>w</sub>*) 0.0339(0.0338). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>||</sup> While this study was underway a similar result appeared; T. Kitamura, L. Zheng, H. Tanizuchi, M. Sakurai and R. Tanaka, *Tetrahedron Lett.*, 1993, **34**, 4055.