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LETTERS

Benzeneseleninic Anhydride Oxidation of 1,2-Diarylethanes and 1,2-Diarylethylenes to 1,2-Diaryldiketones

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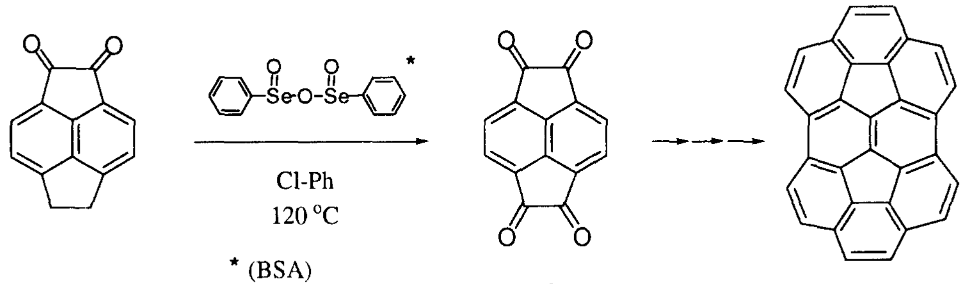
Abstract: 1,2-Diarylethanes and 1,2-diarylethylenes can be oxidized directly to 1,2-diaryldiketones in good yields by reaction with benzeneseleninic anyhdride (BSA) at 120 °C in chlorobenzene.

We have been investigating the synthesis of "buckybowls" which are curved-surface, polynuclear aromatic hydrocarbons having carbon frameworks that can be identified on the buckminsterfullerene surface.[1] In many important syntheses of these compounds by us and others, the acenaphthenequinone moiety has served as one of the key intermediates and so the conversion of acenaphthenes to their respective quinones has become a strategic synthetic goal. After repeated failures and poor results, we recently learned that benzeneseleninic anhydride (BSA),[2,3] known to oxidize benzylic methyl or methylene to carbonyl functions,[4] is an excellent reagent for the conversion of **1** to tetraketopyracene (**2**),[5] an intermediate in the synthesis of the first known semibuckminsterfullerene **3**. We now wish to report new and interesting applications of this reaction that we have encountered in our continuing pursuit of novel buckybowls.



1 **2** **3**

As a precursor to the heterocyclic acenaphthenequinone, we synthesized the previously unknown 4-aza-acenaphthylene **4** by flash vacuum pyrolysis of the corresponding acetylene, and catalytic hydrogenation afforded 4-aza-acenaphthene **5**.[6] Indeed, subsequent treatment of **5** with BSA in chlorobenzene at 120 °C for 72 hours did successfully lead to the quinone **6** in 52% yield.[8] However, while this procedure seems to provide a good route to acenaphthenequinones, our synthetic pathways, as illustrated by the above route, often involve 1,2-diarylalkenes as intermediates necessitating a separate hydrogenation step to obtain the

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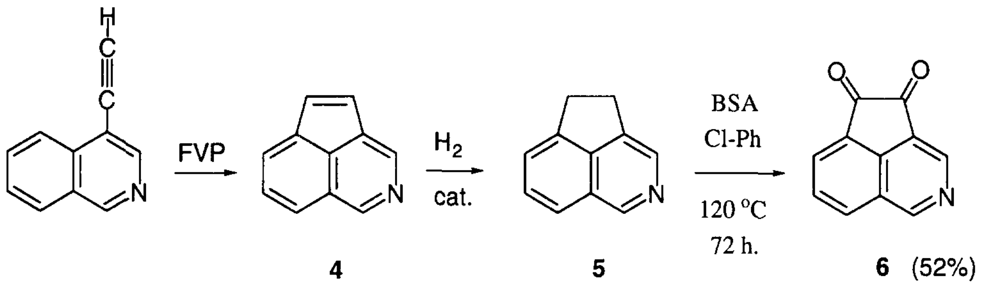
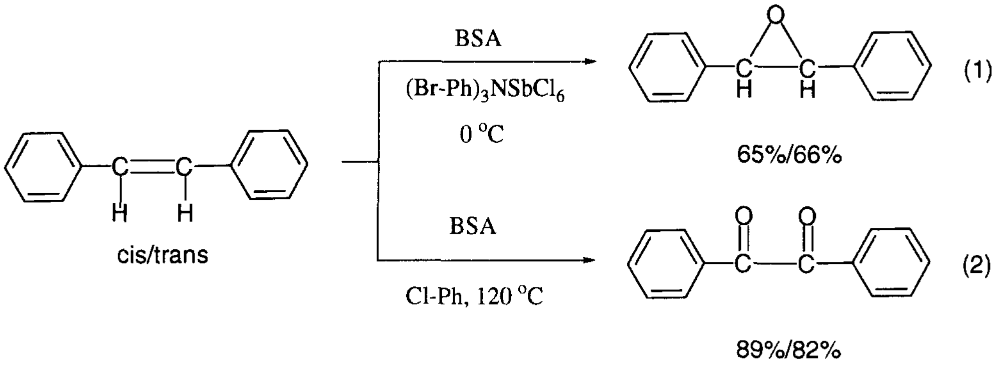


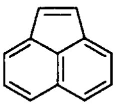
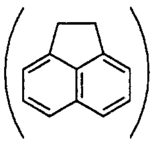
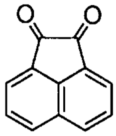
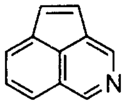
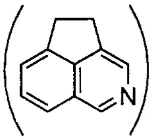
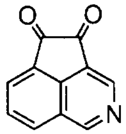
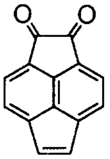
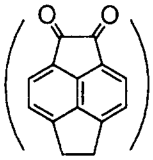
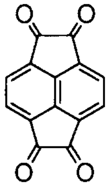
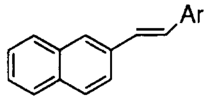
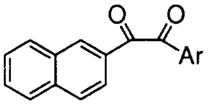
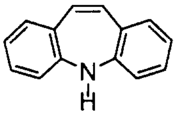
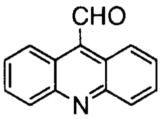
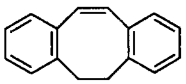
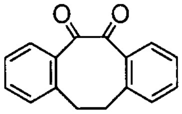
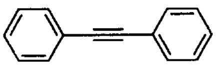
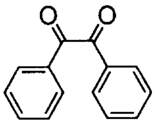
1,2-diarylethanes. For this reason we were prompted to attempt the direct oxidation of diarylalkenes to quinones with BSA. However, rather than risk the rare **4**, we decided to examine the reaction using stilbene, the simplest model, notwithstanding the fact that an earlier report showed that oxidation of both *cis*- and *trans*-stilbene with BSA at 0 °C in the presence of catalytic amounts of tris(4-bromophenyl)aminium-hexachloro-antimonate led to epoxidation[9] (eq. 1). Of course, our conditions are quite different, and when



we reacted either cis or trans stilbene with BSA at 120 °C in chlorobenzene for 8 hours we obtained the desired ketone in excellent yield. This success prompted us to look at the pair of compounds most relevant to our synthetic efforts, acenaphthene and acenaphthylene (Table 1, entry 1). Indeed while they are both oxidized to acenaphthenequinone, the acenaphthylene oxidation required only 2 hours as compared with 24 hours for acenaphthene, and it gave better yields. Having gained confidence in this procedure, we did apply it to the heterocyclic system above and found that 4-aza-acenaphthylene (**4**) reacts in a shorter period of time, 6 hrs as opposed to 72 hrs, and gives better yields, 74% vs. 52%, than our previous reaction with 4-aza-acenaphthene (**5**) (entry 2).

We went on to look at several other systems (Table 1). Tetraketopyracene (**2**) (entry 3) can also be prepared from the unsaturated precursor although there is a trade-off between reaction time and yield. The reaction is almost ten times faster but the yield at 53% is lower than that obtained from the ethane bridged compound (82%). However, as with stilbene, cis/trans mixtures of phenyl 2-naphthyl ethylene and di(2-naphthyl) ethylene (entry 4) proceed in reasonable reaction times and give very good yields of diketones. We obtained our poorest result with 5H-dibenz[b,f]azepine (entry 5) which underwent ring contraction.

Table 1. BSA Oxidation of 1,2-Diarylethylenes (ethanes) in Chlorobenzene at 120 °C.[a]

Entry	1,2-Diarylethylene (ethane)	Product[b]	Rxn Time hrs	Isol. Yield %
1	 		2 (24)	94 (81)
2	 		6 (72)	74 (52)
3	 		8.5 (72)	53 (82)
4	 cis/trans; Ar = phenyl[c] (2-naphthyl)		6 (8.5)	83 (86)
5			4.5	12
6	 [d]		10	25
7	 [c]		20	86

[a] Unless otherwise stated, 2 mol of BSA used per mol substrate. Reagent (Aldrich) is 70% BSA; stoichiometry is 0.33 mol BSA for each methylene unit. See ref. 4. [b] All products gave mp and NMR spectra comparable to those previously reported. See text for entry 2 where products were unknown. [c] 3 mol BSA. [d] 4 mol BSA.

The greater reactivity of diarylethylenes also makes it possible to oxidize the former in the presence of diarylethanes. For example, BSA oxidation of dibenzocyclooctatriene (entry 6) leads to the diketone where reaction has occurred only on the unsaturated part of the central ring although the relatively modest yield is likely due to competitive oxidation of the ethane unit.[10] Finally, this reaction also proceeds smoothly with the additional level of unsaturation provided by diphenylacetylene (entry 7), and although the reaction proceeds a little more slowly, 20 hrs, the yield (86%) is quite good.

Thus BSA oxidation appears to be an excellent method for the oxidation of diarylethanes, diarylethylenes, and even diarylacetylenes, with the option of accomplishing diarylethylene oxidation in either intermolecular or intramolecular competition with diarylethanes or other oxidizable groups.

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3. Ayrey, G.; Barnard, D.; Woodridge, D. T. *J. Chem. Soc.*, **1962**, 2089.
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6. 4-Ethynylisoquinoline[7] (8 g) was pyrolyzed in eight batches at 900 °C under a slow nitrogen bleed according to our usual procedure (see ref. 5b). The crude material was rapidly purified by flash chromatography with methylene chloride/ethyl acetate (10:1) to give 2.95 g (37%) of dark brown solid. ^{1}H NMR δ 9.24 (bs, 1H), 8.76 (bs, 1H), 7.89 (d, 8.1Hz, 1H), 7.81 (d, 6.7Hz, 1H), 7.6 (dd, 6.7, 6.9Hz, 1H), 7.14 (d, 5.2Hz, 1H), 7.08 (d, 5.2Hz, 1H); ^{13}C NMR δ 150.28, 139.1, 138.34, 133.06, 131.4, 129.4, 128.39, 128.16, 126.81, 125.45, 123.38; MS (m/e, rel. intensity): 153 (M$^+$, 100). Hydrogenation (2.95 g) for 2 hrs in a Parr bottle in 150 mL ethyl acetate with 500 mg of 10% Pd/C at 40 psi afforded 2.54 g (85%) **5** as a light brown solid, mp 107-109 °C (methanol). ^{1}H NMR δ 9.07 (bs, 1H), 8.43 (bs, 1H), 7.72 (d, 7.8Hz, 1H), 7.69 (d, 7.8Hz, 1H), 7.55 (d, 6.8Hz, 1H), 7.46 (dd, 5.9, 6.7Hz, 1H), 3.43 (s, 4H); ^{13}C NMR δ 146.0, 144.93, 142.51, 139.52, 136.25, 129.16, 126.70, 123.46, 121.52, 30.12, 28.17; MS (m/e, rel. intensity): 155 (M$^+$, 75), 154 (100), 127 (37). HRMS: calcd for $C_{11}H_9N$, 155.0735; found 155.0737.
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8. A solution of **5** (2.65 g) and benzeneseleninic anhydride (10.5 g) in 250 mL chlorobenzene was heated to 120 °C for 72 hrs. Flash chromatography on silica gel with methylene chloride and then with methylene chloride/ethyl acetate (4:1) gave **6**, 1.62 g, 52%) as an orange solid (mp 225-226 °C, methanol). ^{1}H NMR δ 9.69 (bs, 1H), 9.16 (bs, 1H), 8.44 (d, 8.2Hz, 1H), 8.32 (d, 7.1Hz, 1H), 7.99 (dd, 7.5, 7.8Hz, 1H); ^{13}C NMR δ 187.06, 186.73, 155.51, 147.61, 138.80, 132.25, 129.97, 128.24, 126.56, 126.33, 121.93; MS (m/e, rel. intensity): 183 (M$^+$, 51), 155 (100), 127 (74). HRMS: calcd for $C_{11}H_9NO_2$, 183.0320; found 183.0324.
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10. All starting material is consumed and the product mixture is complex. We also found a number of products with the oxidation of dibenzocyclooctadiene, and the oxidation of dibenzocyclooctatetraene leads, at least in part, to products containing a seven-membered ring. M. D. Clayton and P. W. Rabideau, unpublished results.