

their related high-energy molecules.

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17. (a) The structure of 10,10'-bianthrone was characterized by ¹H-NMR, IR, and EI mass spectrum: ¹H-NMR spectrum (CDCl₃) showed the presence of benzylic protons at 4.78 ppm. Peaks at m/e 386 (M) and m/e 193 (M/2) were observed in EI mass spectrum; (b) For the experimental data of 10,10'-bianthrone, see: O. L. Chapman and K. Lee, *J. Org. Chem.*, **34**, 4166 (1969).
18. (a) The 1 : 1 dimer was identified by ¹H-NMR spectrum (CDCl₃), IR spectrum (KBr) and mass spectrum (EI); Mass (EI), m/e 262 (M) and 194 (M-C₄H₆O, 100%). For this type of 2π_s+2π_s photodimer, i.e., oxetane adduct, see: S. S. Kim, D. Y. Yoo, and I. H. Cho, *Bull. Korean Chem. Soc.*, **9**(4), 257 (1988); (b) [4π_s+4π_s] Photodimer was also isolated as the major product from the photoreaction of anthrone and 1,3-cyclopentadiene in methanol. Mass spectrum (EI), m/e 260 (M), 194 (M-C₅H₆) and 66 (C₅H₆).
19. **5**: ¹H-NMR (CDCl₃) δ 5.68 (bs, -CH=), 2.02 (bs, -CH-) and 1.55 ppm (bs, -CH₂-); Mass (EI), m/e 562 (M), 481 (M-C₆H₉), 401 (m/e 481-80), 321 (m/e 401-80), 241 (m/e 321-80), 161 (m/e 241-80), 81 and 79.
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21. Spectral data of bianthralin: ¹H-NMR (CDCl₃), δ 11.73 (s, 4H, hydroxyl), 7.38 (dd, 4H, aromatic), 6.92 (d, 4H, aromatic), 6.39 (d, 4H, aromatic), 4.60 ppm (2H, benzylic); Mass (EI), m/e 450 (M) and 225 (100%).
22. Fluorescence emission spectra were recorded on a Jasco FP-770 Spectrofluorometer: anthrone (MeOH), λ_{em} 433.3, 452.5 and 517.5 nm (shoulder); 1,8-dihydroxyanthrone (MeOH), λ_{em} 497.5, 525.0 and 565.0 nm; anthranol dimer **3** (MeOH), λ_{em} 432.5 and 455.0 nm (λ_{ex} 375 nm).

Radical Cyclization of α-Diazocarbonyl Compounds

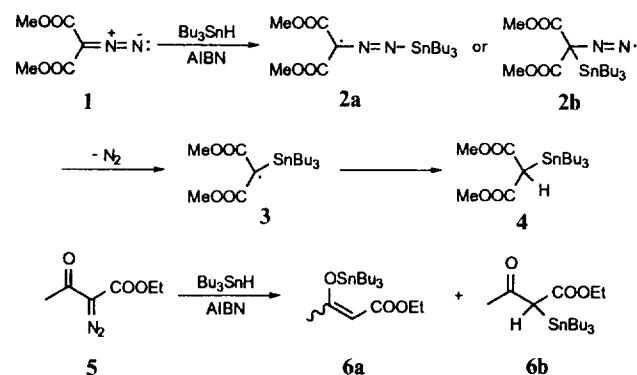
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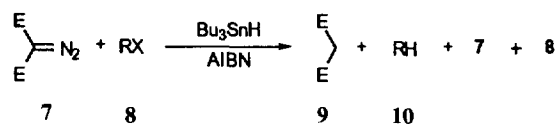
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Synthetic importance of α-diazocarbonyl compounds has been recently recognized in intramolecular carbenoid cyclization¹ and 1,3-dipolar cycloaddition.² However, radical reaction of diazo compounds has received little attention³ and we are unaware of any studies on radical cyclization of α-diazocarbonyl compounds. Our interest in the development of new radical cyclization reactions involving the loss of N₂ prompted us to investigate the possibility of the use of α-diazocarbonyl compounds as radical precursors.⁴ We envisioned that α-diazocarbonyl compounds under radical conditions (Bu₃SnH/AIBN) would generate initially **2a** or **2b**, which would yield **3** by the loss of N₂ as shown in Scheme 1.

Our initial study was carried out with α-diazomalonate and α-diazo β-keto ester. Reaction of **1** with Bu₃SnH/AIBN in refluxing benzene-d₆ for 30 min afforded **4**, suggesting that the diazo group could be served as radical precursors. Similarly, **5** was converted into a mixture of **6a** and **6b** in a ratio of 92 : 8 according to ¹H-NMR analysis.⁵ Furthermore, we examined the relative reactivity of diazomalonate, the iodide and the bromide toward Bu₃SnH/AIBN. The competi-

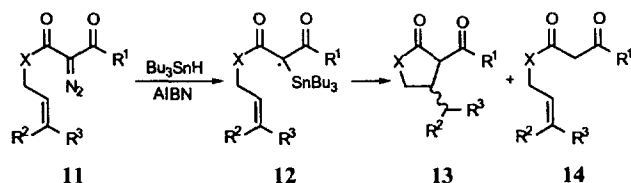


Scheme 1.



E = COOCH ₂ CH ₂ Ph	X = Br	66%	14%	0%	83%
R = (CH ₂) ₁₀ COOCH ₂ Ph	X = I	7%	53%	90%	33%

Scheme 2.



11a: X=CH ₂ , R ¹ =OEt, R ² =R ³ =H	13a: 31%	14a: 41%
11b: X=CH ₂ , R ¹ =OEt, R ² =R ³ =CH ₃	13b: 48%	14b: 21%
11c: X=CH ₂ , R ¹ =OEt, R ² =H, R ³ =Ph	13c: 63%	14c: 14%
11d: X=O, R ¹ =OCH ₂ CH=CH ₂ , R ² =R ³ =H	13d: 43%	14d: 3%
11e: X=O, R ¹ =CH ₃ , R ² =R ³ =H	13e: 26%	14e: 42%

Scheme 3.

tion study was first studied with an equimolar mixture of the diazocarbonyl compound and the bromide using Bu_3SnH (1.0 equiv) and AIBN (0.1 equiv) in refluxing benzene. Although the reduction of the diazo group is faster than that of the bromide as shown in Scheme 2, the bromide was reduced to some extent. The iodide was more reactive than the diazo compound toward Bu_3SnH /AIBN but a small amount of the diazo compound was also reduced. The present results support the reactivity order the iodide>the diazo compound>the bromide.

As shown in Scheme 3, it was expected that the radical

reaction of **11** with Bu₃Sn radical would generate **12** which would undergo radical cyclization to give a mixture of **13** and **14**. The addition of a 0.05 M benzene solution of Bu₃SnH (1.1 equiv) and AIBN (0.1 equiv) by a syringe pump over 3 h to a 0.05 M refluxing benzene solution of **11a** with additional stirring for 1 h afforded a mixture of **13a** and **14a** in 72% yield in a ratio of 43 : 57. The best result was obtained with **11c** in which the cinnamyl group was used as a radical acceptor. Furthermore, the formation of a significant amount **14** may be due to the low reactivity of the stabilized radical **12**.

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5. An equal ratio of E- and Z-isomer was obtained according to ¹H-NMR analysis.