The Tri-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry

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Supporting Information

I. Derivation of Equation 4

1) $dA/dt = -(k_1 + k_2)A$

2) $A = A_0e^{-(k_1 + k_2)t}$

3) $dB/dt = k_1A - k_3B = k_1A_0e^{-(k_1 + k_2)t} - k_3B$

4) $dB/dt + k_3B = k_1A = k_1A_0e^{-(k_1 + k_2)t}$

5) take $B = uv$ then $dB/dt = u(dv/dt) + v(du/dt)$

6) $u(dv/dt) + v(du/dt) + k_3uv = k_1A_0e^{-(k_1 + k_2)t}$

7) $u(dv/dt + k_3v) + v(du/dt) = k_1A_0e^{-(k_1 + k_2)t}$

8) take $dv/dt + k_3v = 0$, then $\int dv/v = -\int k_3dt$

9) $\ln v = \ln v_0 - k_3t$ or $v = v_0e^{-k_3}$

10) $v_0e^{-k_3t}\,(du/dt) = k_1A_0e^{-(k_1 + k_2)t}$

11) $\int du = \int (k_1A_0/v_0)e^{(k_3-k_1-k_2)t}dt$

12) $u = u_0 + [k_1A_0/v_0(k_3 - k_1 - k_2)]e^{(k_3 - k_1 - k_2)t}$

13) $B = uv = u_0v_0e^{-k_3t} + [k_1A_0/(k_3 - k_1 - k_2)]e^{-(k_1 + k_2)} - [k_1A_0/(k_3 - k_1 - k_2)]e^{-k_3t}$

14) For $B_0 = 0$, then

15) $B = (k_1A_0)/(k_3 - k_1 - k_2)[e^{-(k_1+k_2)t} - e^{-k_3t}$

II. Photolysis Conditions

Photolyses were carried out with three filter cells of 2.0 M $NiSO_4$ in 5% H_2SO_4, 0.004 M $SnCl_2$ in 15% HCl and 0.8 M $CoSO_4$ in 5% H_2SO_4. This gave a band pass of 300-0350 nm suitable for selective naphthalene absorption and also for diphenylvinyl absorption in the absence of naphthalene.