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INTRAMOLECULAR PHOTOCYCLOADDITION OF 6,6'-POLYMETHYLENE-BIS(4-METHYL-2-PYRONE)

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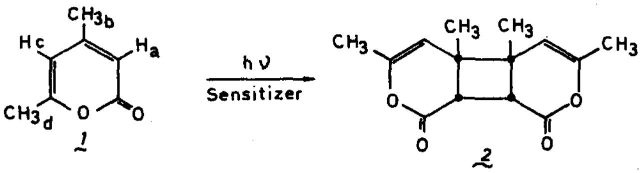
We recently published some examples (1)(2) of intramolecular cycloadditions between non conjugated bichromophoric systems linked by a long flexible chain occuring from the singlet excited state manifold (3). We wish now to report an example of a cyclomerization in such systems from the triplet manifold.

Model compound

Some attention has been given to the photochemistry of 2-pyrone (4-5) and substituted 2-pyrones (6-8). More specifically, the irradiation of the model compound, 4,6-dimethyl-2-pyrone *1* in suspension in benzene resulted in the formation of two (4+4) cycloadducts and two (2+2) cycloadducts (8). However, on sensitization of *1* with benzophenone in benzene or dichloromethane a (2+2) dimer *2* is formed.

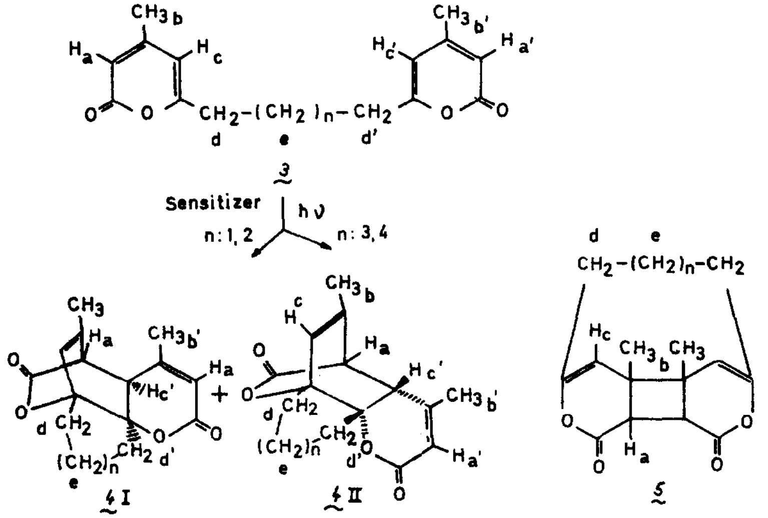


The head to head structure of *2* [m.p. 188°; i.r., KBr $\bar{\nu}_{c=o}$ 1777, 1752 cm^{-1}; n.m.r. CDCl$_3$, TMS, δ : H$_a$ 3.12, H$_b$ 1.11, H$_c$ 4.8, H$_d$ 1.97] is indicated by the large dipole moment (6,89 Db) (6) while endo addition was proved by comparison in the n.m.r. of the position H$_a$ of the dimer with that of the cyclomer (vide infra).

6,6'-Polymethylene-bis(4-Methyl-2-pyrone)

The polymethylene-bis(4-methyl-2-pyrones) *3* were synthesized in analogy with the reported synthesis of 4,6-dimethylpyrone (10). Irradiation of *3a* and

3b in CH_2Cl_2 in the presence of benzophenone or Michler ketone as sensitizer leads to the formation of a 2+4 cyclomer from the triplet manifold. The intramolecular nature of the reaction was established by M.S. While benzophenone sensitization leads to an 2+4 stereoisomer, does the sensitization with Michler's ketone result in the formation of a mixture of two 2+4 stereoisomers. Conversion of one isomer into the other on benzophenone sensitization does not occur. Since in both cases the same bonds reacted only the possibility of endo and exo addition was left. We tentatively assigned the isomer with the lower δ for H_b and the higher δ for H_c, as the one in which the sixmembered ring is at the same side as the double bond formed in the cycloaddition (isomer I; 60% of the mixture). Physical data concerning cyclomers *4I* and *4II* are reported in table I.



3a; n=1 3b; n=2 3c; n=3 3d; n=4

Irradiations of $3\cdot10^{-2}$ mol. solution of *3c* and *3d* in CH_2Cl_2 in the presence of either benzophenone or Michler's ketone as sensitizer result in the exclusive formation of (2+2) intramolecular cycloadduct *5*. The head to head structure of the adduct could be determined by comparison of the dipole moment and of the n.m.r. absorptions of the cyclobutane protons with those of *2*. The physical data concerning the cyclomers *5* are reported in table I. The intramolecular nature of the reaction was proved by mass spectrometry.

TABLE I.

4 (a) I	m.p. 112° $M^{+\cdot}$ 260 i.r. (KBr) $\bar{\nu}_{c=o}$ 1760, 1705 cm^{-1} n.m.r. ($CDCl_3$, TMS, δ) 6.11 (1H,m) H_c; 5.78 (1H,m) $H_{a'}$; 3.48 (1H,t) H_a; 2.81 (1H,m) $H_{c'}$; 2.25 (4H,t) H_d and $H_{d'}$; 2.03 (3H,q) $H_{b'}$; 1.87 (3H,d) H_b; the central methylene lies under the methyl groups.
4 (a) II	(determinated in mixture) n.m.r. ($CDCl_3$, TMS, δ) 5.90 (1H,m) H_c; 5.85 (1H,m) $H_{a'}$; 3.34 (1H,t) H_a; 2.40 (1H,m) $H_{c'}$; 2.25 (4H,t) H_d,$H_{d'}$; 2.05 (3H,q) $H_{b'}$; 1.98 (3H, d) H_b; H_e lies under the methyl groups.
4 (b) I	m.p. 145-146° $M^{+\cdot}$ 274 i.r. (KBr) $\bar{\nu}_{c=o}$ 1758, 1713 cm^{-1} n.m.r. ($CDCl_3$, TMS, δ) 5.87 (1H,m) H_c; 5.85 (1H,m) $H_{a'}$; 3.45 (1H,t) H_a; 2.53 (1H,m) $H_{c'}$; 2.14 (4H,t) H_d,$H_{d'}$; 2.03 (3H,q) $H_{b'}$; 1.84 (3H, d) H_b; 1.65 (4H,m) H_e.
4 (b) II	m.p. 153-155° $M^{+\cdot}$ 274 i.r. (KBr) $\bar{\nu}_{c=o}$ 1746, 1720 cm^{-1} n.m.r. ($CDCl_3$, TMS, δ) 6.09 (1H, m) H_c; 5.93 (1H,m) $H_{a'}$; 3.40 (1H,t) H_a; 2.20 (1H,m) $H_{c'}$; 2.08 (3H,q) $H_{b'}$; 2.02 (3H,d) H_b; 1.90 (4H,t) H_d,$H_{d'}$; 1.59 (4H,m) H_e.
5 (c)	m.p. 116-118° $M^{+\cdot}$ 288 i.r. (KBr) $\bar{\nu}_{c=o}$ 1760, 1720 cm^{-1} n.m.r. ($CDCl_3$, TMS, δ) 4.82 (2H,m) H_c,$H_{c'}$; 3.12 (2H,m) H_a,$H_{a'}$; 2.19 (4H,t) H_d,$H_{d'}$; 1.50 (6H,m) H_e; 1.12 (6H,s) H_b,$H_{b'}$
5 (d)	m.p. 104-105 $M^{+\cdot}$ 302 i.r. (KBr) $\bar{\nu}_{c=o}$ 1760, 1720 cm^{-1} n.m.r. ($CDCl_3$, TMS, δ) 4.80 (2H,m) H_c,$H_{c'}$; 3.12 (2H,m) H_a,$H_{a'}$; 2.20 (4H,t) H_d,$H_{d'}$; 1.38 (8H,m) H_e; 1.13 (6H,s) H_b,$H_{b'}$

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