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UNUSUAL PHOTODIMERS FROM A NAPHTHO-2,4-CYCLOHEPTADIENONE: EVIDENCE FOR TRANS INTERMEDIATES

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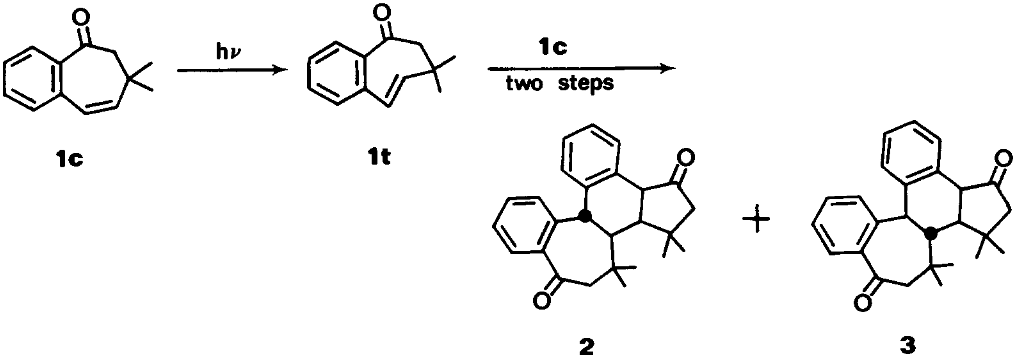
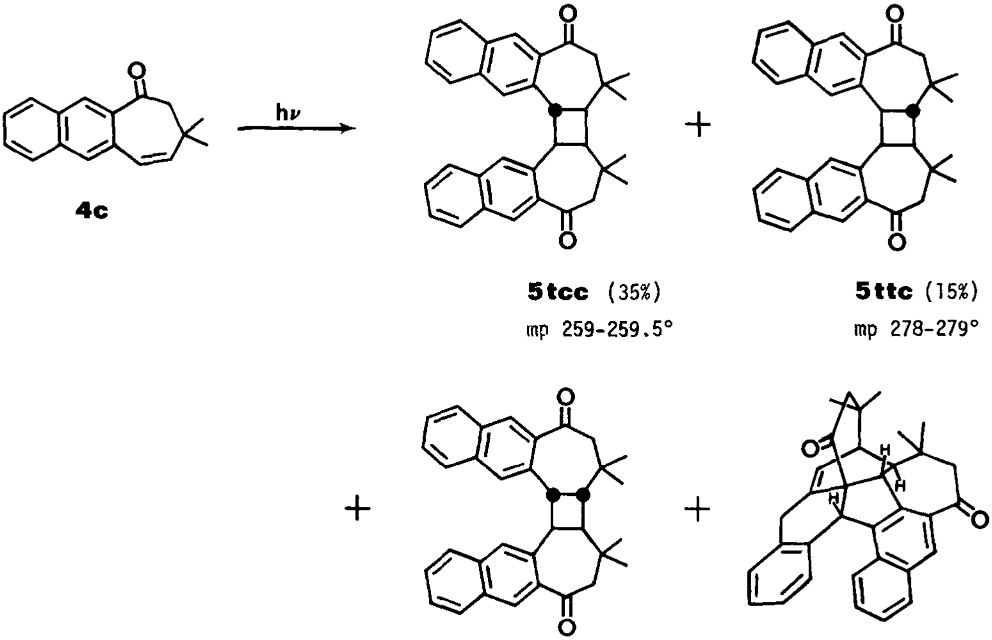
In previous papers[1,2] we showed that irradiation of **1c** in an inert solvent produces two photodimers, **2** and **3**, via a trans intermediate[3] **1t** which can be trapped by furan.[2] We now find that irradiation of naptho-analogs of **1c** does not give dimers which correspond in structure to **2** and **3**, although intermediates analogous to **1t** are formed.



Irradiation of **4c** [4,5] (0.05M in cyclohexane, 450W Hanovia lamp, Pyrex, 4 hr) gave four crystalline photodimers[6] to which we assign structures **5** [7] and **6**. The mass spectra showed that all three stereoisomers of **5** were cyclobutane dimers [the base peak corresponded to P/2 (m/e 236) and the parent peak P had a low intensity (5% of base or less, at m/e 472)]. Dimer **6** was unique, the parent peak (m/e 472) being the base peak. The dimer structures were determined by single crystal x-ray analysis.[8]



4c

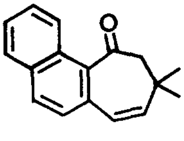
5tcc (35%)
mp 259-259.5°

5ttc (15%)
mp 278-279°

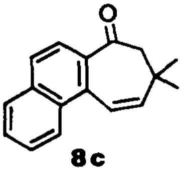
5ctc (7%)
mp >300°

6 (23%)
mp >300°

In contrast with 4c, irradiation of 7c ^{4,5} or 8c ^{4,5} under similar conditions in cyclohexane gave only recovered starting material in nearly quantitative yield. No dimers were

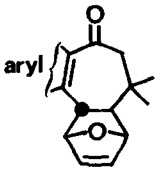


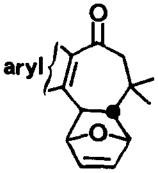
7c



8c

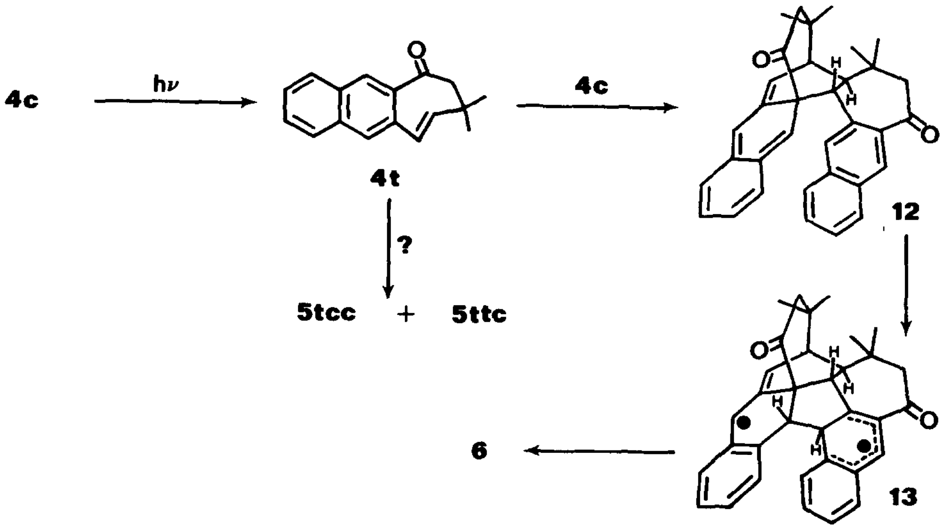
formed. However, irradiation of 4c, 7c or 8c as above but in furan as the solvent gave in each case two crystalline trans cycloadducts (9-11) in good yield.^{5,9,10}





Dienone		mp,°	%		mp,°	%
4c ⟶	9a	129-130	59	9b	171-172	21
7c ⟶	10a	167-168	59	10b	179-180	19
8c ⟶	11a	163-164	41	11b	186-187	28

We conclude that in each case a trans intermediate is formed, analogous to 1t from 1c. In the case of 4t, the unusual trans-fused cyclobutane dimers 5tcc or 5ttc may be formed,[11] or the intermediate may add to the styrene moiety in 4c, to give the cycloadduct 12. This adduct



is fully analogous to the one[12] proposed[2] as an intermediate in the formation of 2 from 1c, except for the additional fused benzene rings. In the previous example[1,2] aromatization was achieved by a 1,3-suprafacial acyl shift. The o-quinone dimethide moiety in 12, however, most likely has some diradical character. The naphthalene ring in 12 is beautifully located for radical attack, which gives 13; the geometry of 13 (from models) is just right for subsequent intramolecular 1,5-hydrogen abstraction, to give 6.

Many unanswered questions remain, but it seems clear that the trans intermediates formed by irradiation of **1c**, **4c**, **7c** or **8c** react similarly toward furan but very differently toward their cis counterparts.[13] This research is continuing.

Acknowledgement. We are indebted to the National Institutes of Health (GM-15997) for financial support.

References and Notes

1. H. Hart, T. Miyashi, D.N. Buchanan and S. Sasson, J. Am. Chem. Soc., **96**, 4857 (1974).
2. H. Hart and M. Suzuki, Tetrahedron Lett., preceding paper.
3. This may be a ground state trans benzocycloheptadienone as shown (**1t**), or an excited state of **1c** which reacts as if it had trans geometry at the double bond.
4. The synthesis of **4c**, **7c** and **8c** is analogous to the described[1] synthesis of **1c**; details will be presented in a full paper.
5. All new compounds gave correct elemental analyses, and spectra in accord with the assigned structures. All yields are of pure, isolated products.
6. Compound **6** deposited as colorless needles during the irradiation and was recrystallized from acetone. The cyclobutane dimers were separated by column chromatography (silica gel 60, EM reagent, >230 mesh, methylene chloride eluent) in the order **5ctc**, **5tcc** and **5ttc**; each was recrystallized from acetone.
7. The designations t or c refer to the trans or cis geometry around the cyclobutane ring, proceeding clockwise from the 'upper left' carbon atom.
8. We are indebted to Dr. Carol Biefeld for the structure of **5tcc** and to Dr. Donald Ward for the other structures; details will be published elsewhere.
9. It was possible to uniquely assign chemical shifts and coupling constants to each methine proton. The structures were obvious from these data; see ref. 2 for the principal arguments used in assigning structures to the analogous benzo adducts.
10. The isomers were separated by column chromatography (silica gel 60, EM reagent, >230 mesh, methylene chloride eluent); the a isomer was eluted before the b isomer; both isomers were recrystallized from hexanes.
11. Compound **5ctc**, which represents only a minor fraction of total products, is the only product which still has cis stereochemistry at what was originally the double bond in the starting material. Other examples of trans-fused cyclobutanes are, of course, well known, especially from enones; for examples and some leading references, see R.M. Bowman, C. Calvo, J.J. McCullough, P.W. Rasmussen and F.F. Snyder, J. Org. Chem., **37**, 2084 (1972).
12. See structure **6** in ref. 2.
13. We speculate that **7t** and **8t** are probably formed in cyclohexane as well as in furan, but that in the former solvent they simply return to their cis isomers.