

A Photoinduced Two Carbon Ring Expansion leading to an Easy Synthesis of γ -Tropolone

Marino Cavazza^a and Francesco Pietra^b

^a *Dipartimento di Chimica e di Chimica Industriale, Università di Pisa, 56100 Pisa, Italy*

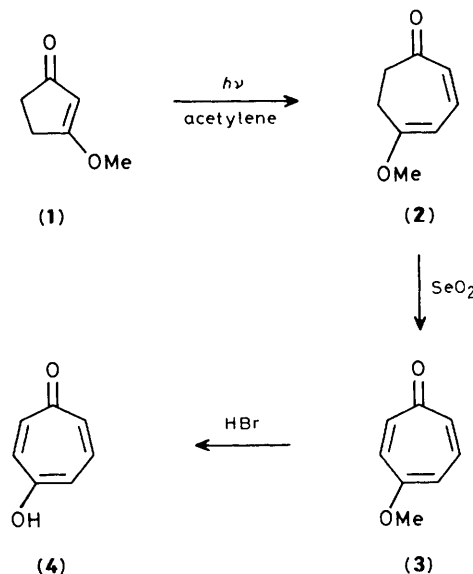
^b *Istituto di Chimica, Università di Trento, 38050 Povo-Trento, Italy*

Irradiation of 3-methoxycyclopent-2-en-1-one (**1**) and an excess of acetylene in MeCN at 0 °C with Pyrex-filtered light from a Hg-lamp gives 5-methoxycyclohepta-2,4-dien-1-one (**2**), which undergoes SeO₂ oxidation to 4-methoxytropone (**3**), a known source of γ -tropolone (**4**); using dideuterioacetylene in place of acetylene, a 3 : 2 mixture of the isomeric 2,3- and 3,4-dideuterio analogues of (**2**) is obtained, suggesting a limitation of this method for substituted γ -tropolones.

Three of the four parent troponoids (troponone and α - and β -tropolone) can be easily synthesized.¹ In contrast, no practical route to the fourth parent troponoid, γ -tropolone, is yet available. In fact, when γ -tropolone is needed in huge amounts, one has still to make recourse to the hydrolysis of 6 β ,7 β -dimethoxytropinone methobromide,² which is very expensive or lengthy to synthesize. Other proposed syntheses of γ -tropolone are impractical, such as either a low yielding process starting with the photocycloaddition of 3-acetoxycyclopent-2-en-1-one^{3a} or a cyclization of diazocompounds giving an unspecified overall yield,^{3b} or, finally, a low yielding solvolysis of 1,4-dihydrobenzyl toluene-*p*-sulphonates.^{3c}

Stimulated by the upsurge of interest in troponoids as synthons,⁴ we have recently devised routes to compounds of this class which are based on the photocycloaddition of cyclopentenones with alkynes. Thus, we have reported efficient synthesis of the otherwise not easily available 3-^{5a} and 4-alkyltropones.^{5b} Continuing our studies,⁵ we now report a novel photoinduced, two carbon ring expansion of cyclopentenones leading to an easy synthesis of γ -tropolone.

A solution of freshly sublimed 3-methoxycyclopent-2-en-1-one (**1**) (easily obtained by the treatment of commercially available cyclopentane-1,3-dione with diazomethane⁶), 1.43 g, in 250 ml of acetonitrile was saturated with acetylene at 0 °C and irradiated through Pyrex with a medium pressure, 125 W, immersion Hg-lamp for 8 h to 19% disappearance of enone (**1**).† Solvent evaporation and t.l.c. of the residue on Merck Kieselgel 60 PF₂₅₄ with light petroleum (b.p. 40–60 °C)–Et₂O (6 : 4) led to 5-methoxycyclohepta-2,4-dien-1-one (**2**),‡ *R*_F 0.60 [0.28 g, 57% yield from reacted (**1**)], besides unreacted enone (**1**), *R*_F 0.15 (1.2 g) (Scheme 1). Dienone (**2**), 0.2 g, was then refluxed for 10 min with 0.18 g of SeO₂ in 5 ml of Bu^tOH under N₂, giving 4-methoxytropone (**3**)^{2a} after t.l.c. with C₆H₆–EtOH (4 : 1), *R*_F 0.57 (0.08 g, 38%).§ Finally, γ -tropolone (**4**)



Scheme 1

was obtained in nearly quantitative yield by the known^{2a} treatment of compound (**3**) with HBr.

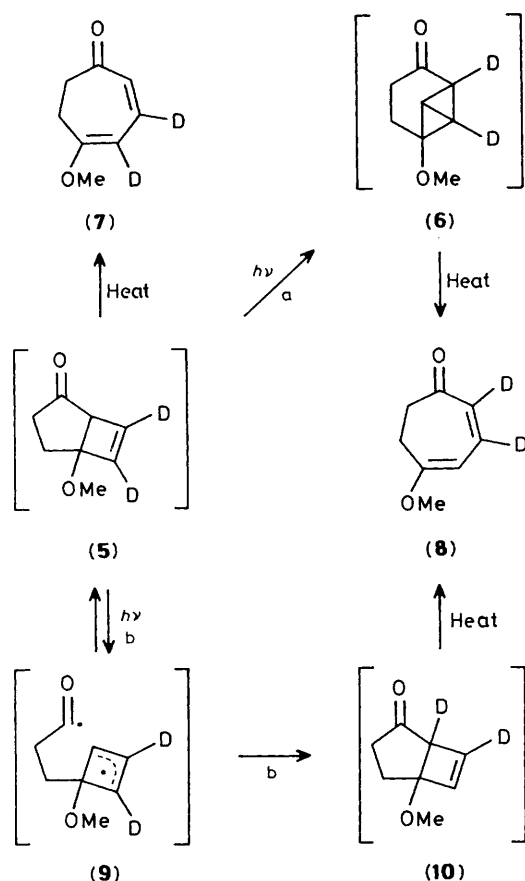
It is likely that this method is largely restricted to the parent, unsubstituted troponoid (**4**), unless the separation of mixtures of isomers is carried out; furthermore, unpredictable substituent effects may lead preferentially to one isomeric substituted analogue of dienone (**2**). In fact, when acetylene was replaced by dideuterioacetylene in the photoprocess of Scheme 1, the olefinic proton resonances of the dienone which was isolated consisted of two sharp multiplets at δ_{H} 5.71 and 5.06, in a 3 : 2 ratio. These two resonances are attributable to 2-H of dienone (**7**) and 4-H of dienone (**8**),¶ respectively, formed in a 3 : 2 molar ratio (Scheme 2). This can be rationalized (Scheme 2) in terms of the (undetected) primary photocycloadduct (**5**) undergoing an electrocyclic opening to give dienone (**7**) in competition with path a, the photorearrangement to give dienone (**8**) via the (undetected) intermediate (**6**).⁴ Alternatively, ring opening of (**5**) to give (**9**) and reclosure to give (**10**),⁷ followed by thermal electrocyclic opening to (**8**) (Scheme 2, path b) affords another rationalization. That the alkoxy group in intermediate (**5**) must be responsible for these mechanisms is suggested by the fact that with either hydrogen^{5a,8} or an alkyl group^{5b} in place of the methoxy

† An excess of enone (**1**) is needed throughout the process in order to protect dienone (**2**) from phototransformations. Probably, the addition, as an internal filter, of an unreactive compound absorbing light in the same region as (**1**) might avoid the use of excess of (**1**). However, when high quantities of γ -tropolone are required, the use of a more powerful Hg-lamp is recommended. Another way which is likely to eliminate such problems would be to irradiate (**1**) selectively by exploiting the coherence of the laser light (M. Zandomeneghi, M. Cavazza, L. Moi, and F. Pietra, *Tetrahedron Lett.*, 1980, **21**, 213).

‡ Oil, satisfactory elemental analysis; δ_{H} (CDCl₃, 60 MHz, rel. to Me₄Si) 6.55 (dd, *J*_{3,2} 12.6, *J*_{3,4} 8.2 Hz, 3-H), 5.71 (d, *J*_{2,3} 12.6 Hz, 2-H), 5.06 (d, *J*_{4,3} 8.2 Hz, 4-H), 3.48 (s, OMe), 2.4 (m, 6-H₂ and 7-H₂); *m/z* 138 (100%, *M*⁺), 110 (87), 109 (51), 95 (69), 79 (36); u.v. λ_{max} (EtOH) 332 nm (log ϵ 3.67); i.r. ν_{max} (neat) 1650 cm⁻¹ (C=O).

§ As all of dienone (**2**) disappeared during this process, it is likely that the yield of 4-methoxytropone (**3**) could be increased on either shortening the reaction time or lowering the reaction temperature or, finally, on adding Bu^tOOH.

¶ What has been interpreted as a 3 : 2 mixture of dienones (**7**) and (**8**), isolated as described above for dienone (**2**), gave satisfactory elemental analysis and mass spectra.



Scheme 2

group, bicyclic compounds of type (5) do not give the (5) \rightarrow (7) process.

It is worth noting that the present method provides conjugated cycloheptadienones having an enol ether function

which may add further synthetic versatility. Actually, fully conjugated cycloheptadienones have been rather difficult to prepare so far.^{1,9}

We thank a referee for suggesting path b in Scheme 2 and both M.P.I. (Progetti di Interesse Nazionale) and C.N.R., Roma, for financial support.

Received, 21st April 1986; Com. 522

References

- 1 F. Pietra, *Chem. Rev.*, 1973, **73**, 293.
- 2 (a) J. Meinwald and O. L. Chapman, *J. Am. Chem. Soc.*, 1958, **80**, 633; (b) M. Cavazza, C. A. Veracini, and F. Pietra, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1915.
- 3 (a) H. Hikino and P. de Mayo, *J. Am. Chem. Soc.*, 1964, **86**, 3582; B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, 1969, **34**, 794; (b) J. Font, S. Serratosa, and J. Vals, *Chem. Commun.*, 1970, 721; (c) O. L. Chapman and P. Fitton, *J. Am. Chem. Soc.*, 1963, **85**, 41.
- 4 J. H. Rigby, *Tetrahedron Lett.*, 1970, 3205; M. Franck-Newmann, F. Brion, and D. Martina, *ibid.*, 1978, 5033; M. E. Garst, V. A. Roberts, and C. Prussin, *J. Org. Chem.*, 1982, **47**, 3969; J. H. Rigby, J. M. Sage, and J. Raggion, *ibid.*, 1982, **47**, 4815; A. E. Greene, M. A. Teixeira, E. Barreiro, A. Cruz, and P. Crabbè, *ibid.*, 1982, **47**, 2533; C. Le Drian and A. E. Greene, *J. Am. Chem. Soc.*, 1982, **104**, 5473; M. Cavazza, G. Morganti, A. Guerriero, and F. Pietra, *J. Chem. Soc., Perkin Trans. 1*, 1984, 199; K. S. Feldman, J. H. Come, A. J. Freyer, B. J. Kosmider, and C. M. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 1327.
- 5 (a) M. Cavazza and F. Pietra, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2283; (b) M. Cavazza, A. Guerriero, and F. Pietra, *ibid.*, 1986, in the press.
- 6 H. O. House and G. H. Rasmussen, *J. Org. Chem.*, 1963, **28**, 26.
- 7 E. P. Serebryakov, S. D. Kulomzina-Pletneva, and A. K. Margaryan, *Tetrahedron*, 1979, **35**, 77.
- 8 M. Zandomeneghi, M. Cavazza, and F. Pietra, *J. Am. Chem. Soc.*, 1984, **106**, 7261.
- 9 E. E. van Tamelen and G. T. Hildahl, *J. Am. Chem. Soc.*, 1956, **78**, 4405; A. M. Becker and R. W. Richards, *Org. Prep. Proceed. Int.*, 1983, **15**, 239 (*Chem. Abstr.*, 1983, **99**, 157876b); H. Hart and M. Weisner, *Tetrahedron Lett.*, 1981, **22**, 3115; L. Blanco, N. Slougui, and J. M. Conia, *ibid.*, 1981, **22**, 645; J. E. Baldwin and B. M. Broline, *J. Am. Chem. Soc.*, 1982, **104**, 2857.