

Two Methoxycarbonylketen Equivalents as Dienophiles in the Diels–Alder Reaction

Indranil Gupta and Peter Yates*

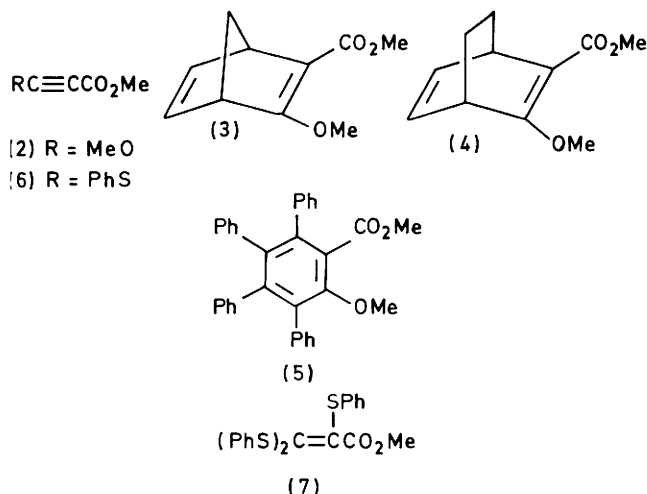
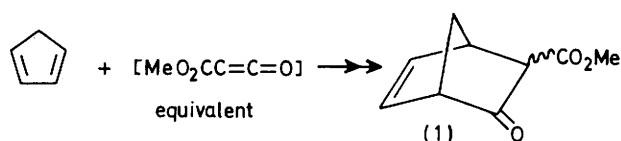
Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Methyl methoxypropiolate and methyl (phenylthio)propiolate give Diels–Alder adducts with 1,3-dienes; the adducts with cyclopentadienes give methyl 3-oxobicyclo[2.2.1]hept-5-ene-2-carboxylates on hydrolysis.

It is well known that the synthesis of bicyclo[2.2.1]hept-5-en-2-ones *via* Diels–Alder reactions with cyclopentadienes requires the use of ‘keten equivalents’ as dienophiles since ketens themselves undergo 1,2-cycloaddition reactions with cyclopentadienes. A variety of keten equivalents, such as α -acetoxyacrylonitrile and α -chloroacrylonitrile have been used,

but less attention has been paid to alkoxycarbonylketen equivalents,^{1–3} even though the β -keto-esters (**1**) to which their adducts can give rise (Scheme 1) are useful in synthesis. We report the preparation and Diels–Alder reactions of two such equivalents.

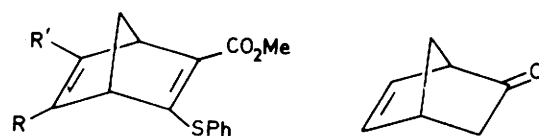
Methyl methoxypropiolate (**2**), prepared (25–30%) by



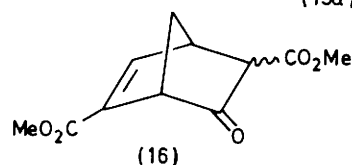
methoxycarbonylation of methoxyacetylene,³ gave the adduct (3) with cyclopentadiene in boiling benzene; this adduct, on hydrolysis with methanolic HCl at room temperature, gave the β -keto-ester (1) as a mixture of epimers (50%).¹ Similar reactions of (2) with cyclohexa-1,3-diene and tetraphenylcyclopentadienone gave the adduct (4) (30%) and the decarbonylated adduct (5) (60%), respectively. Because of the hazards involved in the preparation of methoxyacetylene, its low yield, and its poor dienophilicity, we replaced the ether residue by a sulphide group.[†]

Methyl (alkylthio)propiolates have been referred to⁶ as dienophiles in the Diels-Alder reaction but not as methoxycarbonylketen equivalents. We first attempted to prepare methyl (phenylthio)propiolate (6) by reaction of the anion of methyl propiolate with diphenyl disulphide (lithium di-isopropylamide, tetrahydrofuran, -70°C); this led, however, to methyl tris(phenylthio)acrylate (7) as the major product. Successful preparation of (6) was achieved in 65% yield by methoxycarbonylation of the anion of (phenylthio)acetylene (MeLi, ClCO_2Me , -10°C).⁷

Reaction of (6) with cyclopentadiene in boiling benzene gave the Diels-Alder adduct (8) in 90% yield, which was converted into the β -keto-ester (1) by treatment with mercuric chloride in aqueous acetonitrile.⁸ This in turn was demethoxycarbonylated with 1,4-diazabicyclo[2.2.2]octane in boiling xylene⁹ to give bicyclo[2.2.1]hept-5-en-2-one (9), identified as its 2,4-dinitrophenylhydrazone (60%). Reaction of (6) with a 1.2:1 mixture of 1- and 2-(trimethoxymethyl)cyclopentadiene (10)¹⁰ gave in 65% yield a mixture consisting primarily (ca. 90%) of the adducts (11) and (12) (ca. 4:1) formed from (10b) alone. Hydrolysis of these adducts with 0.1 M HCl at $0-5^\circ\text{C}$ gave the diesters (13) and (14), respectively. These were identical to two of the adducts formed on reaction of (6) with



- (8) R = R' = H
(11) R = C(OMe)₃, R' = H
(12) R = H, R' = C(OMe)₃
(13) R = CO₂Me, R' = H
(14) R = H, R' = CO₂Me
- (9)
- (10a) R = C(OMe)₃
(15a) R = CO₂Me



- (10b) R = C(OMe)₃
(15b) R = CO₂Me

methyl 1- and 2-cyclopentadienecarboxylate (15);¹¹ two adducts of (6) with (15a) were also formed, one as a major product. Treatment of (13) with mercuric chloride in aqueous acetonitrile gave the keto-diester (16) as a mixture of epimers (60%).⁸

Although methyl methoxypropiolate (2) does not appear to be very promising as a methoxycarbonylketen equivalent in Diels-Alder reactions, methyl (phenylthio)propiolate (6) is comparable with other such equivalents^{1,2} and complements them in that conversion of the adducts into the corresponding β -keto-esters does not require treatment with bases.

We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

Received, 27th July 1982; Com. 888

References

- P. Chamberlain and A. E. Rooney, *Tetrahedron Lett.*, 1979, 383.
- B. M. Trost and G. Lunn, *J. Am. Chem. Soc.*, 1977, **99**, 7079.
- B. R. Vogt, J. Bernstein, and F. L. Weisenborn, Fr. P. (Demande) 2,138,112, 1973 (*Chem. Abs.*, 1973, **79**, 18452q).
- Cf. J. Nieuwenhuis and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, 1958, **77**, 761.
- H. Staundinger and H. Becker, *Chem. Ber.*, 1917, **50**, 1016.
- R. Raap and R. G. Micetich, *Can. J. Chem.*, 1968, **46**, 1057; J. Bonnema and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, 1960, **79**, 1137.
- W. E. Parham and P. L. Stright, *J. Am. Chem. Soc.*, 1956, **78**, 4783.
- Cf. E. J. Corey and J. I. Shulman, *J. Org. Chem.*, 1970, **35**, 777.
- Cf. B. S. Huang, E. J. Parish, and D. H. Miles, *J. Org. Chem.*, 1974, **39**, 2647.
- P. Yates and I. Gupta, *J. Chem. Soc., Chem. Commun.*, 1981, 449.
- C. J. Bouboulis, *J. Org. Chem.*, 1967, **32**, 3540; D. Peters, *J. Chem. Soc.*, 1959, 1042; H. K. Wiese, U.S. P. 2,781,395, 1957 (*Chem. Abs.*, 1957, **51**, P13913i); K. Ziegler, H. Froitzheim-Kühlhorn, and K. Hafner, *Chem. Ber.*, 1956, **89**, 434.

[†] Ethyl ethoxypropiolate, whose preparation is less hazardous than that of (2), underwent elimination of ethylene⁴ in boiling benzene to give an ethoxycarbonylketen dimer.⁵