# A Photochemical Approach to Methyl-substituted 5-Oxabicyclo[2.1.0]pent-2-enes (Dewar Furans)

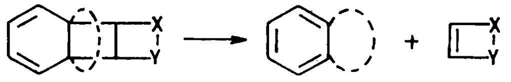
**Ronald N. Warrener, Ian G. Pitt, and Richard A. Russell**

*Chemistry Department, Australian National University, Box 4 G.P.O., Canberra, A.C.T., 2601, Australia*

U.v. irradiation of the *N*-methylsuccinimide-containing propellanes (**12**) and (**13**) yields the cyclopropenyl ketones (**19**) and (**20**) logically derived by the intermediacy of the Dewar furans (**15**) and (**16**).

The 1,2-photoaromatisation reaction[1] (Scheme 1) has proved eminently suitable for introducing a $\pi$-bond into a variety of strained molecules, especially those involving a 4-membered ring.[2,3] An outstanding application of this photofragmentation reaction has been to produce cyclobutadiene,[3] a result which attests to its ability to yield high-energy species. We report the results of applying this reaction to the generation of Dewar furans, a rare species where only a single member has yet been captured and that, one of relatively low reactivity (see later).[4]

In selecting the photosubstrates (**12**) and (**13**) for this work we included a pinching group[5] to ensure stability of the bicyclo[4.2.0]octa-2,4-diene moiety[6] and to aid the fragmentation step. The syntheses of (**12**) and (**13**) outlined in Scheme 2 are novel and utilise the *N*-methylsuccinimide ring system in this pinching role, rather than the related succinic anhydride as reported by others,[7] since the *N*-substituted imides are less prone to competitive photofragmentation.[8] The choice of the Dewar benzene intermediates (**6**) and (**7**), while daring,† was entirely successful and led to high yields of the adducts (**8**)‡ and (**9**)‡ where the presence of the activated maleimide functionality in (**6**) and (**7**) ensured the correct site-selectivity upon reaction with 2,5-dimethyl-3,4-diphenylcyclopentadienone.



**Scheme 1**

Photoaromatisation of the tetramethyl Dewar furan precursor (**12**) occurred readily to yield the phthalimide (**14**) and the oily cyclopropenyl ketone (**19**; 56% yield after distillation; quantitative by $^{1}$H n.m.r.).§ Similarly the trimethyl Dewar furan precursor (**13**) yielded the related cyclopropenyl ketone (**20**). In each case no evidence for the Dewar furan (**15**) and (**16**) could be obtained either by low-temperature $^{1}$H n.m.r. spectroscopy or by attempted trapping with dienes.

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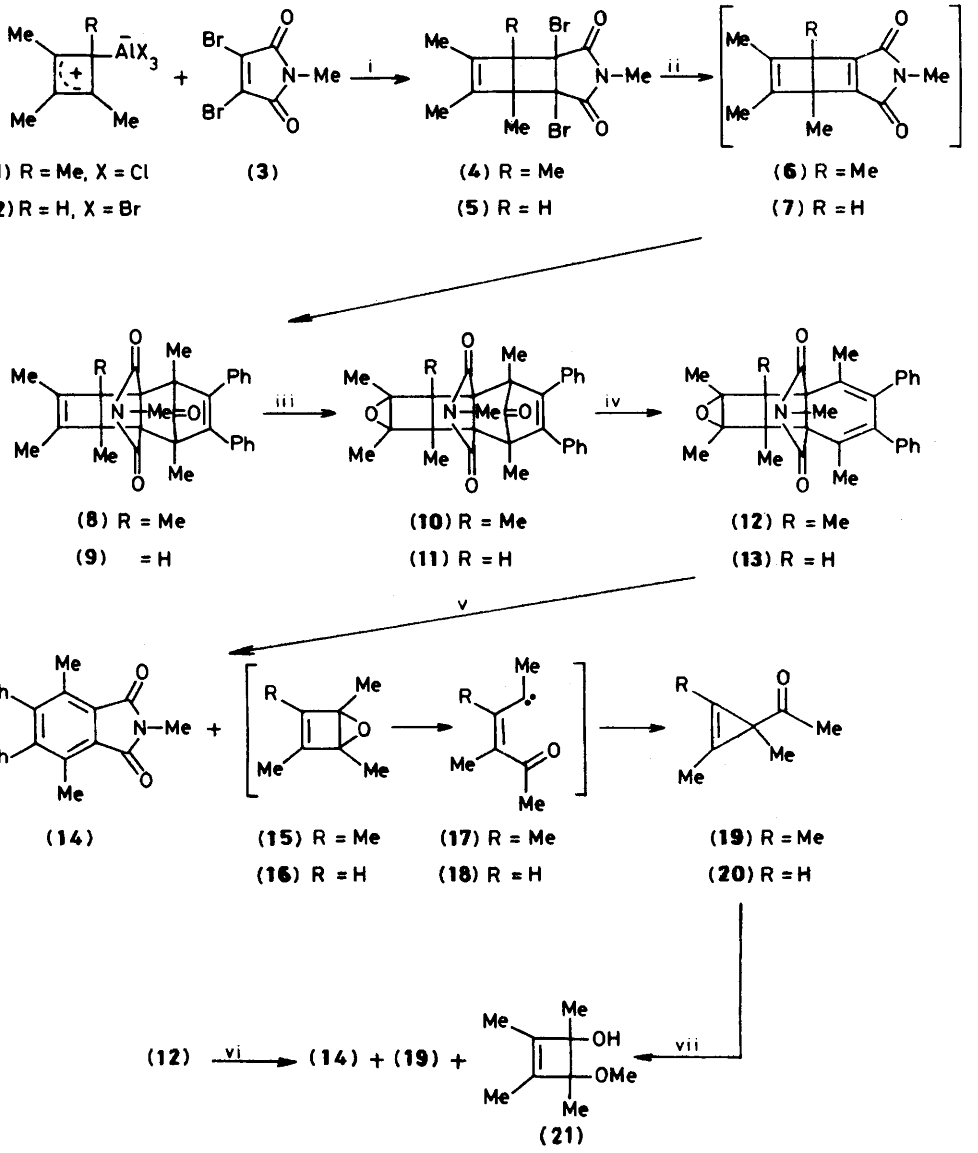
† These systems contain the reportedly unstable (R. L. Cobb and J. E. Mahan, *J. Org. Chem.*, 1977, **42**, 1948) and hitherto unknown 3-azabicyclo[3.2.0]hept-1(5)-ene-2,4-dione moiety. The trimethyl cyclobutadiene complex (**2**) (H. Hogeveen and D. M. Kok, *Tetrahedron Lett.*, 1980, 659) had not previously been employed in cycloaddition reactions; under our conditions, complete regiospecificity was observed.

‡ All new crystalline compounds gave satisfactory n.m.r., mass spectral, and microanalytical data; m.p.s (% yields); (**4**) 201—207 °C (80); (**5**) 140—142 (82); (**8**) 195—196 (77); (**9**) 158—160 (75); (**10**) 208—210 (89); (**11**) 199—201 (89); (**12**) 201—202 (90); (**13**) 194—195 (94); (**14**) 217—218 (100); (**19**) oil (56); (**20**) oil (40); (**21**) oil (55). Stereochemical assignments have not been made for compounds (**8**)—(**13**).

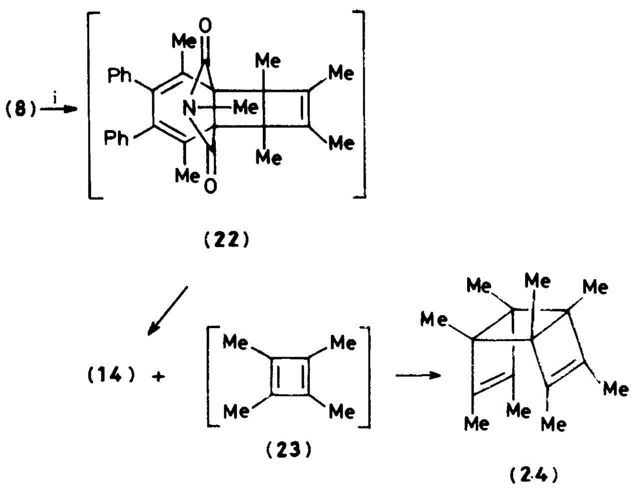
§ $^{1}$H N.m.r.: (**19**) ($CDCl_3$): $\delta$ 1.17 (3H, s, Me), 1.80 (3H, s, COMe), and 2.02 (6H, s, 2 × vinyl Me); (**20**) ($CD_3COCD_3$): $\delta$ 1.14 (3H, s, Me), 1.73 (3H, s, COMe), 2.17 (3H, d, *J* 1.3 Hz, vinyl Me), and 6.82 (1H, q, *J* 1.3 Hz, 2-H); (**21**) ($CDCl_3$): $\delta$ 1.33 (3H, s, Me), 1.36 (3H, s, Me), 1.55 (3H, q, *J* 1.2 Hz, Me), 1.60 (3H, q, *J* 1.2 Hz, Me), and 3.32 (3H, s, OMe). $^{13}$C N.m.r.: (**19**) ($C_6D_6$): $\delta$ 8.16 (2 × vinyl Me), 17.04 (Me), 25.52 (COMe), 36.96 (C-3), 110.63 (C-1, C-2), and 210.21 (CO); (**21**) ($CDCl_3$): $\delta$ 7.01, 8.76 (2 × vinyl Me); 16.06, 19.46 (2 × Me); 52.72 (OMe); 81.44, 85.69 (C-1, C-4); and 142.01, 142.41 (C-2, C-3).



**Scheme 2.** *Reagents:* i, dimethyl sulphoxide, $CH_2Cl_2$, 0 °C for (**1**), −78 °C for (**2**); ii, Zn–Ag couple, tetrahydrofuran at reflux in presence of 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer; iii, 3-chloroperbenzoic acid, $CH_2Cl_2$, 20 °C; iv, diglyme, reflux; v, acetone, −90 °C, 254 nm, 2 h, *ca.* $4 \times 10^{-2}$ M; vi, MeOH, −20 °C, 254 nm, work up at <20 °C; vii, MeOH, 20 °C, 30 min.

The failure of the trapping experiments may simply indicate the poor dienophilicity of the π-bond in these Dewar furans.¶ Alternatively it may reflect their very rapid conversion into cyclopropenes under the reaction conditions. This latter explanation is plausible since the only reported Dewar furan, which is fully substituted with thermally stabilising trifluoromethyl groups,[9] has been shown by Lemal[4] to undergo isomerisation ($t_{\frac{1}{2}}$ 20 min at 95 °C) to a cyclopropenyl ketone corresponding to (**19**).

In an attempt to obtain evidence for the intermediacy of the vinyl carbene species (**17**) in the conversion of the Dewar furan (**15**) into the cyclopropene (**19**), irradiation of (**12**) was carried out in methanol solution. A new cyclic product was obtained (55%), but control experiments revealed that it was derived from the cyclopropenyl ketone (**19**). The cyclobutene



**Scheme 3.** i, *Reagents:* i, tetrahydrofuran, −105 °C, 254 nm, 2 h.

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¶ A Dewar furan containing an activated π-bond has been successfully trapped by cycloaddition onto furan, I. G. Pitt, R. A. Russell, and R. N. Warrener, *J. Chem. Soc., Chem. Commun.*, 1984, following communication.

structure (**21**) is proposed for this product on the basis of spectral data.§ Thus evidence for the explicit formation of Dewar furans in these reactions has not been obtained, but the ability of the related compound (**8**) to yield [*via* the diene (**22**)] tetramethylcyclobutadiene (**23**) [isolated as the *syn*-dimer (**24**)][7] upon irradiation (Scheme 3) firmly establishes that high-energy species can be produced by this protocol.

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