The Generation and Trapping of a Novel Dewar Furan

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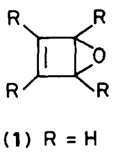
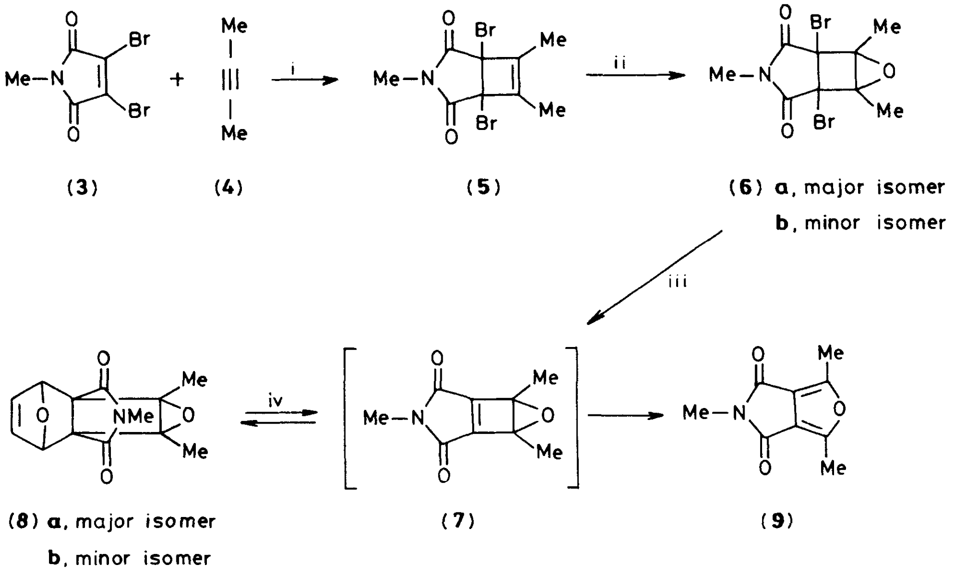
2,4,7-Trimethyl-7-aza-3-oxatricyclo[3.3.0.0^{2,4}]oct-1(5)-ene-6,8-dione (**7**), a derivative of the rarely observed Dewar furan ring-system, has been prepared by Zn–TiCl$_4$ debromination of dibromide (**6**) and trapped *in situ* with furan.

Dewar furan (**1**) has been estimated by CNDO/2 calculations to be 202 kJ mol^{-1} less stable than its heteroaromatic counterpart, furan.[1] In keeping with this prediction the recent photochemical approach to the synthesis of methyl substituted Dewar furans was unsuccessful, not because of the inherent failure of the method, but because of the low stability of the representative Dewar furans studied.[2] Indeed the only stable Dewar furan isolated to date[3] is (**2**), which is fully substituted by trifluoromethyl groups, a feature known to offer special stability to strained ring-systems.[4] For this reason we directed our attention to the synthesis of a Dewar furan containing activating substituents on the π-bond to facilitate trapping.



(**1**) R = H
(**2**) R = CF$_3$

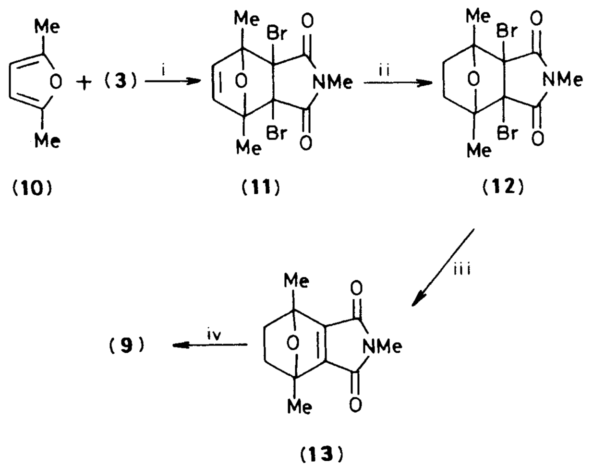
The Dewar furan (**7**) was selected as our target molecule, but in so doing we were conscious of the report that 3-azabicyclo[3.2.0]hept-1(5)-ene-2,4-dione, a subunit in (**7**), had been considered to be too strained for normal existence.[5] However, we have shown that systems containing this sub-unit can be prepared (but not isolated) and display high dienophilic reactivity at the π-bond,[2] a property useful in the present study. We now show that the Dewar furan (**7**) can be produced and in so doing report only the second example of this rare ring-system.



Scheme 1. *Reagents:* i, *h*ν, acetone, 0 °C, 11 h; ii, 3-chloroperbenzoic acid, CHCl$_3$, 60 °C, 4 days; iii, tetrahydrofuran, furan, Zn powder, TiCl$_4$, reflux, 2 h; iv, f.v.p., packed tube, 500 °C, 0.01 Torr.

The immediate precursor required for our synthesis was the dibromide (**6**).[†] This was prepared by the sequence outlined in Scheme 1, where the first step involves photochemical [2 + 2] cycloaddition of dibromomaleimide (**3**) onto but-2-yne (**4**) to form the cyclobutene (**5**). Epoxidation of (**5**) with 3-chloroperbenzoic acid was slow but the required precursor was formed in 79% overall yield as a 3 : 1 mixture of isomers (**6**).[‡] Debromination of this mixture was the key step in our synthesis and was achieved by treatment of (**6**) with zinc powder and a catalytic amount of titanium tetrachloride.[6][§] The target molecule (**7**) was too unstable to be isolated, but could be trapped in adduct form by effecting the debromination of (**6**) in the presence of furan. Two isomeric furan adducts (ratio 10 : 1) were isolated in 46% yield and separated by layer chromatography. The spectral characteristics of these adducts supported the assigned structures (**8**) where the C_{2v} symmetry was clearly evident.[¶]

In a further attempt to isolate the Dewar furan (**7**) the mixture of adducts (**8**) was subjected to flash vacuum pyrolysis (f.v.p.) at 500 °C. Two products were isolated and identified as furan and the bicyclic derivative (**9**). The structure of (**9**) was confirmed by independent synthesis as outlined in Scheme 2.



Scheme 2. *Reagents:* i, CCl_4, 70 °C, 7 h; ii, H_2, 10% Pd on C, ethyl acetate, 12 h; iii, Zn powder, Et_2O, reflux, 4 h; iv, f.v.p., packed tube, 550 °C, 0.01 Torr.

Compound (**9**) can be formally derived *via* the Dewar furan (**7**), but not exclusively so. The mechanistic details of this transformation are presently being investigated.

[†] All new compounds gave satisfactory n.m.r., mass spectral, and microanalytical data; m.p.s (% yields); (**5**) 94—95 °C (50); (**6a**) 154—155 (62); (**6b**) 172—173 (17); (**8a**) 155—157 (41); (**8b**) 188—189 (5); (**9**) 164—166 (90); (**11**) 156—158 (86); (**12**) 131—133 (96); (**13**) 113—115 (82).

[‡] The stereochemistry of these isomers has not been determined; ^{1}H n.m.r.: δ ($CDCl_3$), (**6a**), 1.71 (6H, s, 2 × Me) and 3.07 (3H, s, NMe); (**6b**) 1.54 (6H, s, 2 × Me) and 3.13 (3H, s, NMe).

[§] The dibromide (**6a**) is debrominated much faster than (**6b**) under the reaction conditions. Neither isomer is debrominated with Ag–Zn couple or Zn powder.

[¶] ^{1}H N.m.r.: δ ($CDCl_3$), (**8a**), 1.58 (6H, s, 2 × Me), 2.81 (3H, s, NMe), 5.10 (2H, t, J 1.0 Hz, allylic), and 6.46 (2H, t, J 1.0 Hz, olefinic); (**8b**), 1.41 (6H, s, 2 × Me), 2.97 (3H, s, NMe), 5.14 (2H, t, J 1.0 Hz, allylic), and 6.68 (2H, t, J 1.0 Hz, olefinic).

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