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THE CORRECTION ON THE STRUCTURE OF DIELS-ALDER REACTION PRODUCTS OF FURAN DERIVATIVES WITH MALEIC ANHYDRIDE

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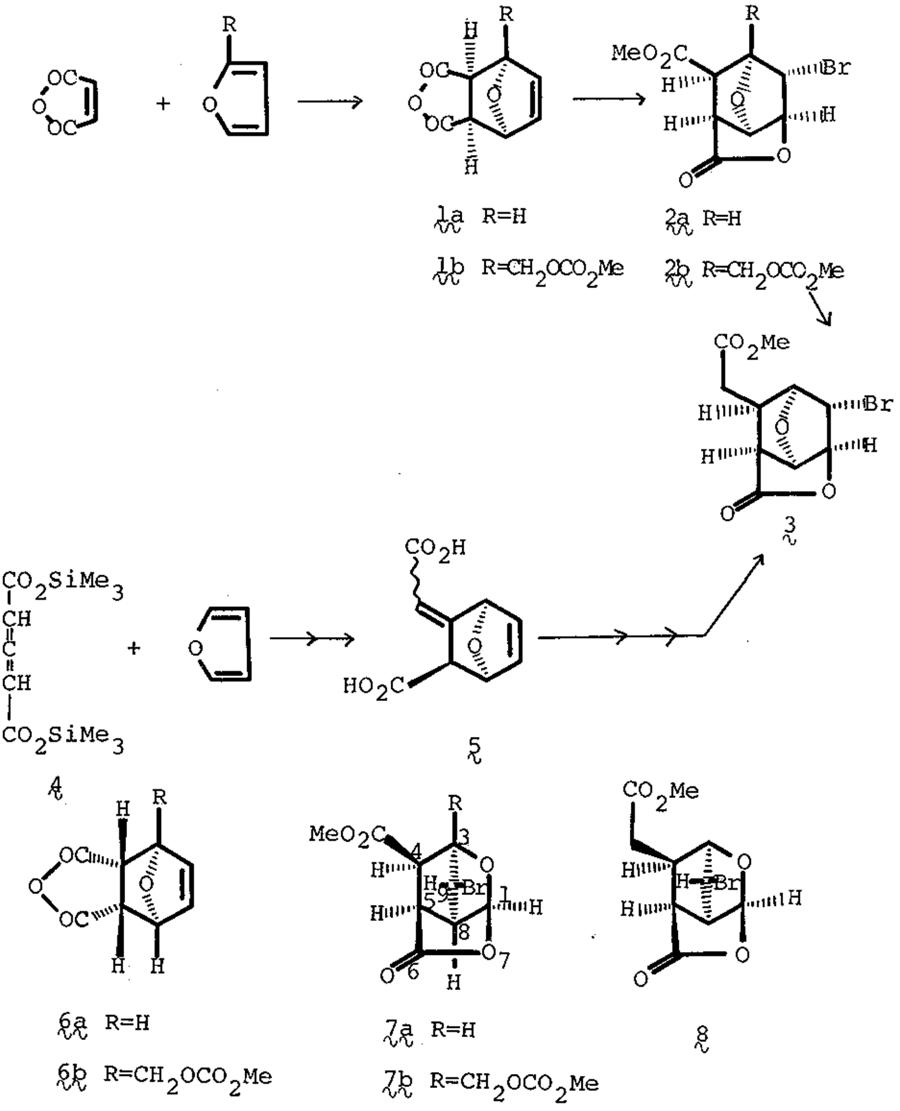
The structure of Diels-Alder adducts and related compounds prepared from furans and maleic anhydride was re-examined by the ^{13}C-NMR spectroscopy and our tentative structures were revised.

In a previous paper[1], we have reported a syntheiss of 3,8-epoxy-7-keto-6-oxabicyclo[3.2.1]octane derivatives (**2** and **3**) starting from furans and maleic anhydride.

Afterwards, we have investigated an alternative synthesis of **3** from allene derivative (**4**) and furan *via* the Diels-Alder adduct **5** as starting materials as described in the preceding papers[2], and found that the product obtained by the former method was different from that of the latter reaction. Therefore, the structures in the previous paper were re-examined by ^{13}C-NMR spectroscopy, and

Scheme


1a R=H
1b R=CH2OCO2Me
2a R=H
2b R=CH2OCO2Me
3
4
5
6a R=H
6b R=CH2OCO2Me
7a R=H
7b R=CH2OCO2Me
8
MeO2C
Br
CO2Me
CO2SiMe3
CO2H
HO2C

here we have revised the structures **1**, **2** and **3** to **6**, **7** and **8**, respectively.

The ^{13}C-NMR spectrum (δ in DMSO-d_6) of the halolactone **7a** showed a methine carbon at 82.9 due to C_3 and an unusually deshielded one at 104.4 due to C_1 together with seven resonances at 175.1, 168.3 53.7, 52.3, 51.2, 47.8 and 39.5. These data ruled out the structure **2a**[3] reported in the previous paper and supported **7a** proposed by Woodward.[4] Moreover, the ^{1}H-NMR spectrum (δ in $CDCl_3$) revealed the C_1-proton at 6.08 (1H) as a doublet having $J = 3$ Hz in addition to the C_4-proton at 3.28 (1H, dd, $J = 2$ and 12 Hz) and the C_5-proton at 3.06 (1H, dd, $J = 5$ and 12 Hz), indicating both hydrogens to have <u>cis</u>-relationship.

Similarly, the lactone **7b** exhibited the methine carbon due to the C_1-position at 104.7 in the ^{13}C-NMR spectrum (δ in DMSO-d_6: 175.0, 167.6, 154.4, 86.4, 63.8, 55.1, 53.4, 52.9, 51.9, 46.5 and 41.4) and one of C_1-proton at 6.06 (1H, d, $J = 3$ Hz) in the ^{1}H-NMR spectrum.

Therefore, the structures **1** and **3** should be also revised to **6** and **8**, respectively.

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