

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

Toshio Suzuki, Akiko Tomino, Seiko Kagaya,
and Katsuo Unno

Department of Pharmacy, Akita University Hospital,
Hondo, Akita 010, Japan

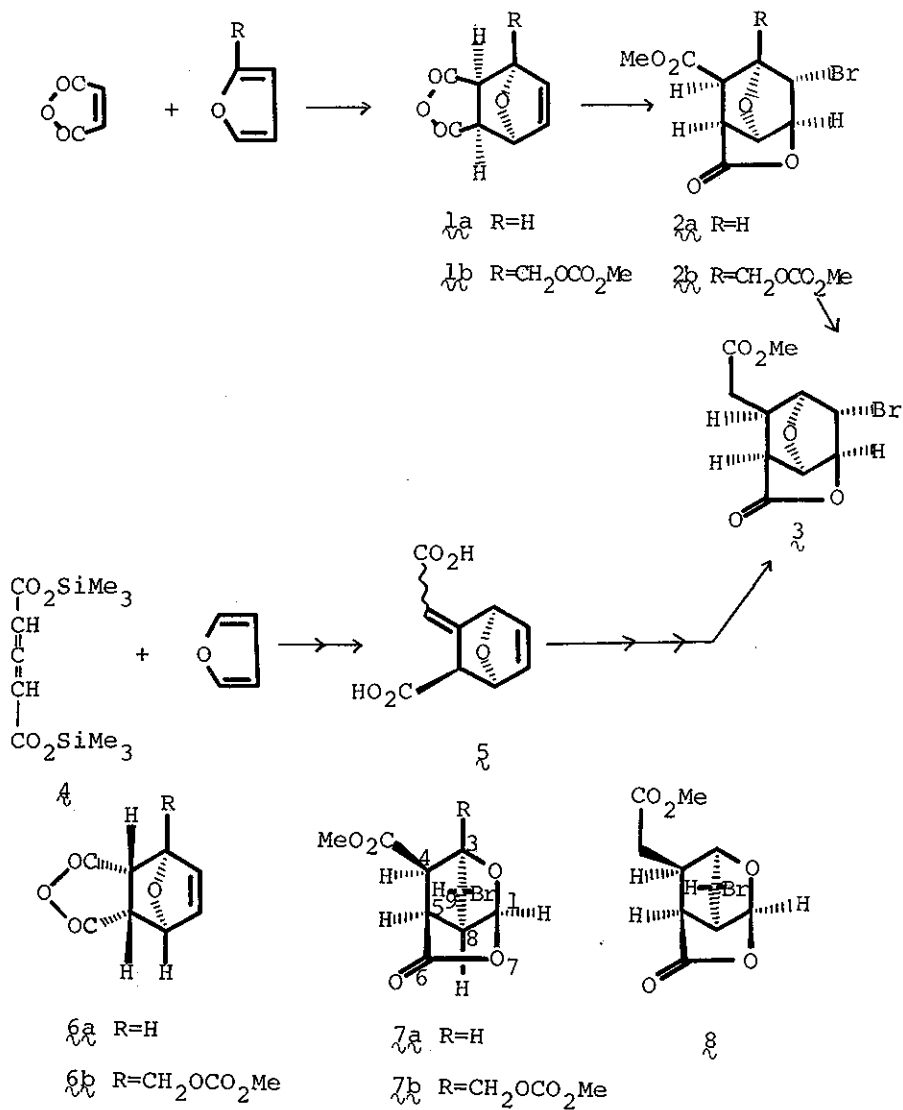
Tetsuji Kametani^{*}, Masataka Ihara, and Tamiko Takahashi
Pharmaceutical Institute, Tohoku University,
Aobayama, Sendai 980, Japan

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 paper¹, we have reported a synthesis 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 papers², 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



here we have revised the structures $\mathfrak{1}$, $\mathfrak{2}$ and $\mathfrak{3}$ to $\mathfrak{6}$, $\mathfrak{7}$ and $\mathfrak{8}$, respectively.

The ^{13}C -NMR spectrum (δ in DMSO-d_6) of the halolactone $\mathfrak{7a}$ 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 $\mathfrak{2a}^3$ reported in the previous paper and supported $\mathfrak{7a}$ proposed by Woodward.⁴ Moreover, the ^1H -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 cis-relationship.

Similarly, the lactone $\mathfrak{7b}$ 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 ^1H -NMR spectrum.

Therefore, the structures $\mathfrak{1}$ and $\mathfrak{3}$ should be also revised to $\mathfrak{6}$ and $\mathfrak{8}$, respectively.

ACKNOWLEDGEMENT

We thank Dr. K. Fukumoto and Dr. K. Ogasawara, Pharmaceutical Institute, Tohoku University, for their kind suggestion and discussion on the structure of the Diels-Alder products.

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Received, 5th October, 1978