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ON THE STRUCTURES OF ADDUCTS BETWEEN 3-METHOXYCARBONYLMETHYLENE-2-OXOINDOLINE AND CYCLOPENTADIENE

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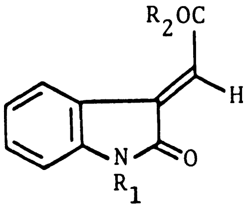
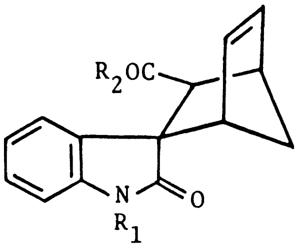
The structure and stereochemistry of the Diels-Alder adducts between 3-methoxycarbonylmethylene-2-oxoindoline and cyclopentadiene are discussed on the basis of the spectral and chemical data.

As an extention of the dimerization reaction of 3-acetonylidene-2-oxoindoline (1a) shown by A. W. Johnson et al.,$^{1)}$ the Diels-Alder reaction of 3-acylmethylene-2-oxoindoline (1a,b) has been demonstrated to be one of the facile synthetic methods for spiro-oxindole derivatives. However, the structures of adducts between (1a or 1b) and cyclopentadiene have not clearly been determined.$^{2,3)}$

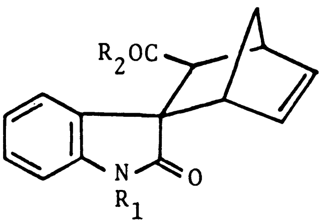
In this paper, we wish to report definite evidence on the structures of adducts between 3-methoxycarbonylmethylene-2-oxoindoline (1c)$^{4)}$ and cyclopentadiene.



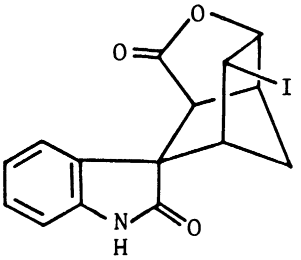
(1a,b,c)



(2a,b,c)
(4): R_1=H, R_2=OH



(3a,b,c)
(6): R_1=H, R_2=OH



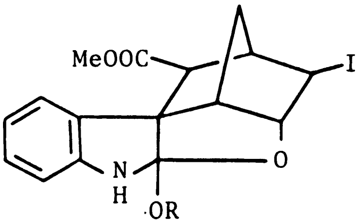
(5)

[a: R_1=H, R_2=Me, b: R_1=Ac, R_2=ϕ, c: R_1=H, R_2=OMe]

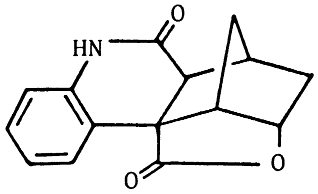
Cycloaddition of cyclopentadiene to (1c) proceeded very smoothly either in benzene and in EtOH at 40°C to afford crystalline adducts (2c, 1.5 parts) and (3c, 1 part) in good yields. When the 1:1 mixture of (2c) and (3c) was refluxed in toluene for 2 h, the ^{1}H NMR spectrum of the reaction mixture showed signals due to (2c) and (1c), probably formed by decomposition of (3c), indicating that the main product (2c) [mp 204.5°C; $C_{16}H_{15}NO_3$(m/e 269(M^+))] would be a thermally more stable isomer than another one (3c) [mp 146.5°C; $C_{16}H_{15}NO_3$(m/e 269(M^+))].

The following iodolactonization reaction were carried out to clarify the stereochemistry of (2c) and (3c). When the carboxylic acid (4) obtained from (2c) was treated with iodine-potassium iodide complex in 0.5 M aq. sodium bicarbonate at r.t., it rapidly gave a crystalline product (5) [mp 251.5°C(decomp.); $C_{15}H_{12}NO_3I$(m/e 381(M^+)); δ($CDCl_3$) 2.36(1H, br.d, J=12Hz), 2.68(1H, d, J=2Hz), 3.01(1H, br.d, J=5Hz), 3.40(1H, br.d, J=12Hz), 3.47(1H, br.s), 4.69(1H, d, J=2Hz), 5.31(1H, br.d, J=5Hz)] in quantitative yield, which showed a γ-lactone absorption band at 1778 cm^{-1} in its

IR spectrum. Reduction of (5) [Zn-AcOH in MeOH] followed by esterification [CH_2N_2 in MeOH] regenerated the starting material (2c) in ∿80% yield. These chemical reactions indicate that the methoxycarbonyl group in (2c) is located on the same side with the double bond. On the other hand, another carboxylic acid (6) obtained from the minor adduct (3c) gave two iodine containing compounds (7)$^{5)}$ [mp 288°C; $C_{16}H_{16}NO_4I$(m/e 413(M^+)); ∿60% yield] and (8) [mp 198°C; $C_{17}H_{18}NO_4I$(m/e 427(M^+)); ∿15% yield] by the same lactonization reaction at 40°C followed by esterification [CH_2N_2 in MeOH]. The major product (7) was further transformed quantitatively to 2-quinolone derivative (9)$^{6)}$ [mp 293°C; $C_{15}H_{13}NO_3$(m/e 255(M^+)); ν(KBr) 1772 cm^{-1}; δ(Py-d_5) 1.35(1H, br.d, J=11Hz), 1.70(1H, br.d, J=11Hz), 1.71(2H, br.s), 3.16(1H, br.d, J=6Hz), 3.24(1H, m), 3.28(1H, br.s), 4.79(1H, br.t, J=6Hz)] by reduction [Zn-AcOH in MeOH, r.t.]. On the same reduction, the minor product (8) gave another 2-quinolone derivative (10)$^{6)}$ [$C_{16}H_{15}NO_3$(m/e 269(M^+)); ν(KBr) 1727, 1665 cm^{-1}; δ($CDCl_3$) 1.43(2H, br.s), 3.07(1H, br.s), 3.53(2H, br.s), 3.66(3H, s), 6.37(1H, br.d, J=7Hz), 6.53(1H, br.d, J=7Hz)], which was further transformed to 4-methoxycarbonyl-2-quinolone (11) [mp 242-243°C]. These transformations indicate that the double bond in (6) is located on the same side with the lactam carbonyl in oxindole ring.



(7):R=H
(8):R=OMe



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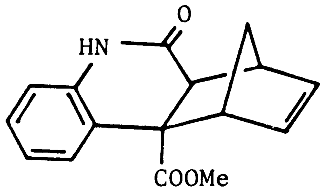
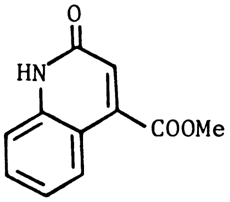


(10)



(11)

REFERENCES AND NOTES

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2. C. G. Richards and M. S. F. Ross, Tetrahedron Lett., 4391 (1968).
3. T. Kato, H. Yamanaka,and H. Ichikawa, Chem. Pharm. Bull., 17, 481 (1969).
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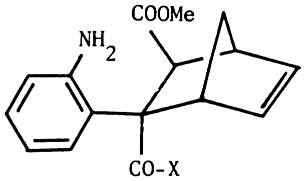
5. This compound is not so stable and is occasionally contaminated with a small amount of iodo-γ-lactone derivative convertible to (9) by Zn reduction.
6. The conversion from (7) to (9) or (8) to (10) should proceed via an intermediate (12a) or (12b), but it should be noted that no (3c), one of plausible products from (12b), could be detected.



(12a): X=OH
(12b): X=OMe

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