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UNUSUAL ANNULATION REACTION OF AN α,β-UNSATURATED KETONE

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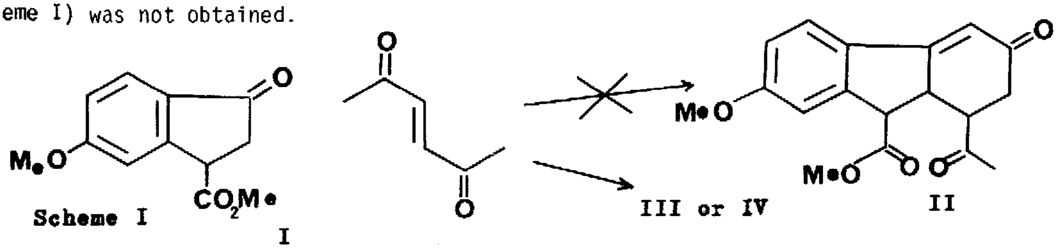
Summary. An unsusual 2,3 cyclopentaindanone (III) was obtained, presumably as a result of a mixed Michael and Stobbe condensation, in the course of an attempted Robinson annulation.

The Robinson annulation reaction is a useful method in the preparation of cyclic α,β-unsaturated ketones [1] and in the litterature many exemples of reactions were found between oxoindanes and methyl-vinyl ketones [2] leading to the classical expected results. However, in attempts to react the oxoindane (I) with 2,5-hexenedione in order to produce the oxofluorene (II) as a potential precursor for gibberelins, the desired unsaturated ketone (Scheme I) was not obtained.

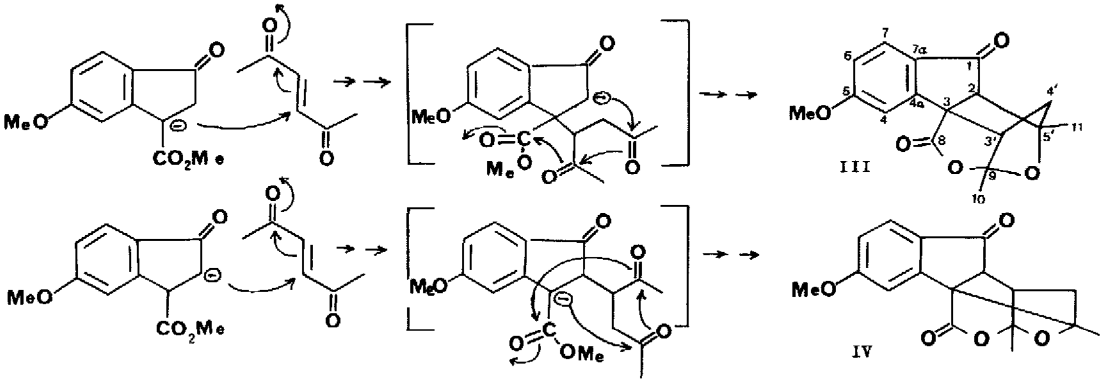


Scheme I

The oxoindane (I) was prepared following House et al. [3] and the reaction with 2,5-hexenedione was carried out in sodium methoxide/methanol at room temperature. We obtained a single product mp 204-5° ; $C_{17}H_{16}O_5$ (M^+ = 300.310). The uv spectrum (λ_{max}^{EtOH} 223 nm ; ε = 15,700 ; 268 nm ; ε = 15,600 ; 285 nm ; ε = 11,700 and 293 nm ; ε = 9,800) of the reaction product and the one of oxoindane (I) were superimposable, indicating that the oxoindane moiety is retained in the product. This was confirmed by the ir spectrum (ν = 1720, and 1600 cm^{-1}), an additional band at 1780 cm^{-1} being indicative of an additional five-membered lactone ring.

The presence of the lactone group in the ir spectrum, the absence of signal corresponding to benzylic protons and the ABCD systems noticed in the ^1H nmr ($CDCl_3$, 400 MHz) spectrum, as well as ^{13}C nmr data (Table 1), support two plausible structures (III) and (IV), without possible discrimination.

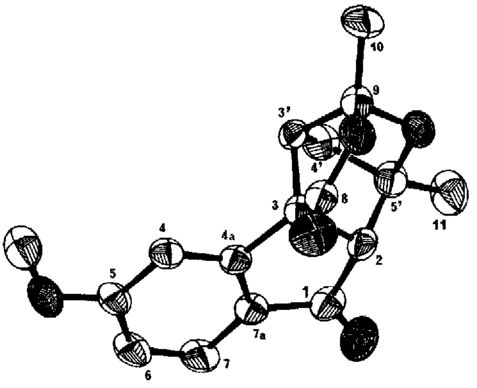
The formation of a product (III) could be explained if we suppose the initial formation of an α-aryl carbanion from the oxoindane substrate (Scheme II). On the other hand, (IV) could be obtained if the reaction proceeds formerly via the α-ketonic carbanion (Scheme III).



In order to settle the correct structure (III) or (IV), for the substance isolated, an X-ray analysis was undertaken. Crystals are monoclinic, space group $P2_1/c$ (Z=4) with the following parameters (Å) : a = 13.24 ; b = 14.45 ; c = 7.69 and β = 95°3. Using an automatic four circle diffractometer, 2169 structural factors were measured above the 2σ background level ($I > 2\sigma(I)$). The structure was solved with the aid of the multisolution technique and refined to a final R factor of 0.09 (thermal factors were anisotropic for the heavy atoms and kept isotropic for hydrogen atoms). It corresponds to the postulated structure III, and the course of this unusual reaction follows therefore the scheme II.

Table 1. Significant ^{13}C and ^{1}H nmr signals of (III)

^{13}C					
n°	δ(mult)	n°	δ(mult)		δ (mult, J)
C_1	197.3 s	C_9	111.5 s	2(D)	3.07(s,broad)
C_2	63.3 d	C_{10}	21.9 q	3'(C)	2.9 (d, 2Hz)
C_3	56.5 s	C_{11}	16.1 q	4'(B)	1.82(dt, 12; 1.5 Hz)
C_4	109. d	C_{12}	55.8 q	4'(A)	1.46(dd, 12; 1.5 Hz)
C_{4a}	150.9 s	$C_{3'}$	56.5 d	4	6.99(d, 2.5 Hz)
C_5	166.1 s	$C_{4'}$	38.4 t	6	7.05(dd, 8.5; 2.5Hz)
C_6	117.8 d	$C_{5'}$	88.3 s	7	7.71(d, 8.5 Hz)
C_7	126. d			9	4.83 (s)
C_{7a}	132. s			10	1.73 (s)
C_8	175.3 s			11	1.69 (s)



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References

1. F.J. Quillin and R. Robinson, J.Chem.Soc., 1097 (1938) : M.E. Jung, Tetrahedron, 32, 3 (1976).
2. K. Mori, M. Shiozaki, N. Itaya, M. Matsui and Y. Sumiki, Tetrahedron, 25, 1293 (1969) ; H.J. Loewenthal and S. Schatzmiller, Tetrahedron Lett., 3115 (1972) ; H.O. House, J.K. Melillo and F.J. Sauter, J.Org.Chem., 38, 741 (1973).
3. H.O. House, J.K. Larson, and H.C. Muller, J. Org. Chem., 33, 961 (1968).

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