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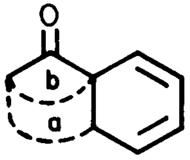
PHOTOCHEMISTRY OF HOMOCONJUGATED KETONES: 2-(CARBOMETHOXY)SPIRO[5.5]UNDECA-1,3-DIEN-7-ONE.[1]

Jakob Oren, Leah Schleifer, Uri Shmueli and Benzion Fuchs*

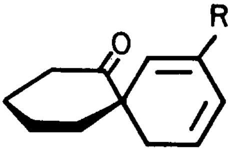
Department of Chemistry, Tel-Aviv University, Ramat-Aviv 69978, Tel-Aviv, Israel

Abstract. The direct and sensitized irradiation of the title compound (2c) was studied with particular attention to its oxa-di-π-methane rearrangement, the product of which is of notable structural and synthetic interest. X-ray diffraction data of the final product (8) are given to support structural assignments.

The photochemistry of homoconjugated carbonyl compounds is subject of vigorous experimental and theoretical study in recent years.[2] We have looked into various of its aspects and presently we are conducting a comprehensive study of $\beta,\gamma,\delta,\epsilon$-unsaturated carbonyl compounds with judiciously juxtaposed carbonyl and 1,3-diene chromophores, the electronic interplay of which is of considerable interest in the context of their spectroscopic and photochemical behaviour. Specifically we are examining 1-acyl-2,4-cyclohexadienes (1) with various, free and biased geometries.[3] Thus, in the 1a series, we have reported on the photochemical behaviour of 2,3,8,9-tetrahydroinden-1-one[4] and of its 2-oxa derivative[5] and in the 1b series we have most recently dealt with certain spiro[5.5]undeca-1,3-dien-7-ones such as 2 a & b[3], focussing our attention on their particularly interesting oxa-di-π-methane (ODPM) rearrangements.[1,6] We report now on the photochemistry of Danishefsky's 2-(carbomethoxy)spiro[5.5]undeca-1,3-dien-7-one (2c).[3,7]



1

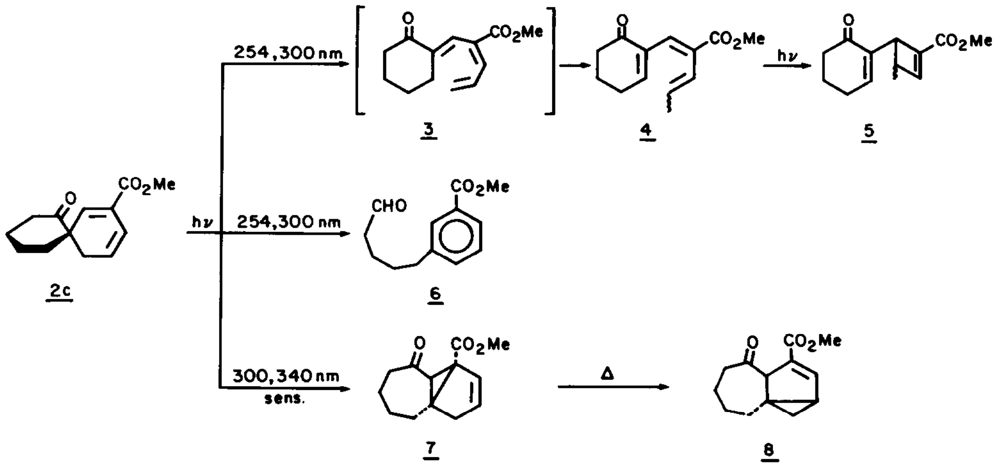


2	a	b	c
R:	H	Me	CO$_2$Me

The results of various direct and sensitized irradiations are summarized in Scheme 1.[8] On direct irradiation at 254 nm in cyclohexane, the main photochemical primary process after ca. 75% conversion is cyclohexadiene electrocyclic opening as judged from isolations of stereoisomeric mixtures of 4 (25%) and 5 (35%) (3 could be observed only by NMR analysis of the crude product mixture). A second, minor process is α-cleavage which leads to the aromatic ester-aldehyde (6)(5%). The yield of 6 is, as expected, better (10%) at 300 nm where 5 (25%)

is also isolated but now the major product is the oxa-di-π-methane rearrangement product 11-carbomethoxy-trans-tricyclo[5.4.0.0^{7,11}]undec-9-en-2-one (7) (60%)[8]; at 340 nm, 7 is exclusively and quantitatively formed. Its configurational assignment gained strength from the fact that (7) rearranges thermally with complete stereoselectivity ($\Delta H^{\ddagger}$ 26 kcal/mol, $\Delta S^{\ddagger}$ 2 cal/deg) to its [5.4.0.0^{7,9}] isomer (8), the oxime of which was analyzed by X-ray diffraction and its structure is displayed in Figure 1.

SCHEME 1



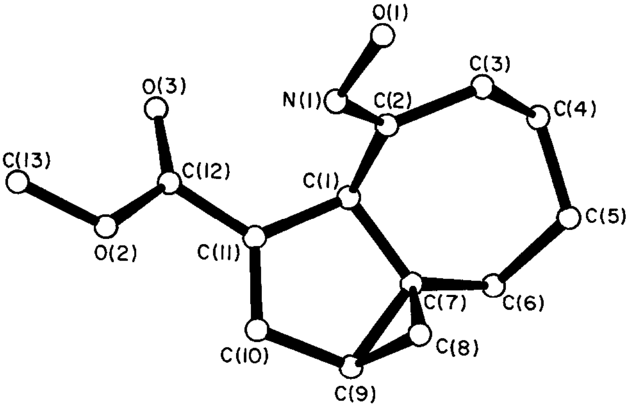


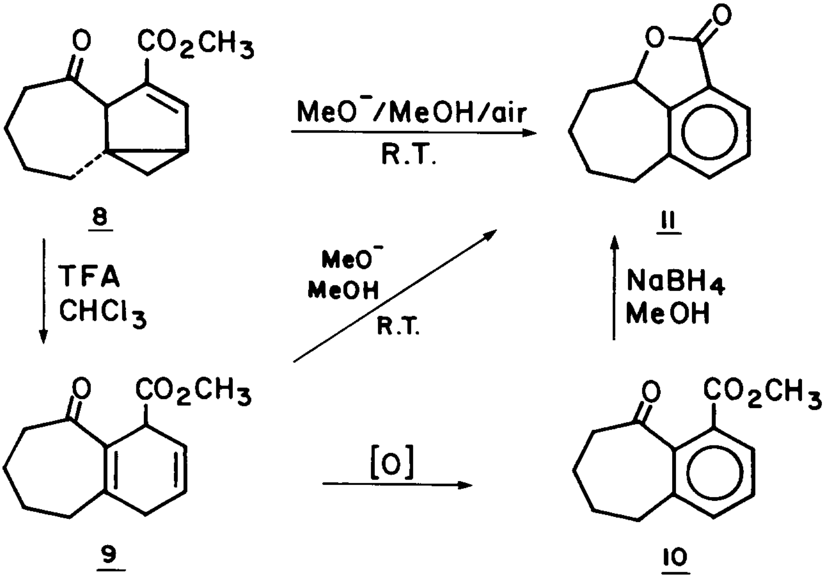
Figure 1. Molecular structure of the oxime of 11-carbomethoxy-trans-tricyclo[5.4.0.0^{7,9}] undeca-10-en-2-one (8).

The oxime of 8, $C_{13}H_{17}NO_3$, M.W.=235, crystallizes in the monoclinic system, space group $P2_1/c$, with four molecules in the unit cell. Intensity data were collected on a CAD4F diffractometer with graphite-monochromatized Mo radiation, in the range: $1° \leqslant \theta \leqslant 27°$. The $\theta/2\theta$ scan technique was used. 2536 reflections were measured, including 2056 independent ones with $I > 3\sigma(I)$. The structure was solved by direct methods using MULTAN78[9] and was refined with a local modification of ORFLS.[10] The final discrepancy factors are $R = 0.042$ and $R_w = 0.062$ for 2052 reflections and 222 parameters.[11] Four strong reflections were excluded from the refinement.

We could show (in low temperature irradiations) that 8 is not a photochemical primary product[1] and 7 is exclusively formed. This can be reasonably attributed to an increased electron density at position 2 in 2c due to the conjugation with the carbomethoxy group. A linear Stern-Volmer plot (at 340 nm) indicated that the excited state involved is clearly a triplet state. Irradiations in presence of acetone and other sensitizers (down to 2-acetonaphthone) lead also quantitatively to 7, putting the lowest triplet energy of 2c around 56 kcal.

One of the attractive features of this work is the chemistry of the rearrangement product (8) which provides a convenient synthetic avenue to the benzocycloheptenone system (Scheme 2). Thus acid treatment of 8 rearranges it to 9 which is easily oxidized by air to 10. The ultimate product, however, is the lactone 11 which can be obtained by base treatment of either 8 or 9 or by $NaBH_4$ reduction of 10.[8]

SCHEME 2



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11. The atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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