Photocycloaddition of Benzophenone to α-Angelicalactone and Thermal Rearrangement of the Product

R. A. Bolívar, M. L. Tasayco, C. Rivas and V. Leon

Centros de Química y de Física, Instituto Venezolano de Investigaciones Científicas, (IVIC), Apartado 1827, Caracas 1010-A, Venezuela.

α-Angelicalactone dissolved in thiophene in the presence of benzophenone was irradiated with uv light in order to find out if the unsaturated lactone behaves either as an olefin capable of yielding a [2 + 2] adduct with the heterocycle or if it rather reacts as a substrate for the excited benzophenone. The isolation of two isomeric oxetanes indicates that the latter is the preferred reaction pathway. One of the oxetanes undergoes an interesting thermal rearrangement.

It is well known that citraconic anhydide and 2,3-dimethylmaleic anhydride undergo [2 + 2] cycloaddition reactions with thiophene and furan in the presence of benzophenone as the sensitizer (1). It is also well known that 2,3-dihydrofuran undergoes photocycloaddition reaction with benzophenone to form an oxetane (2).

α-Angelica lactone may be viewed as a compound possessing a double bond which may be capable of undergoing [2 + 2] cycloadditon reactions with heterocyclic systems in a fashion similar to that of the above mentioned anhydrides or else it may behave as a derivative of dihydrofuran to yield an oxetane. Since this apparent dual character of α-angelicalactone has not been explored as yet an experiment was carried out in an attempt to find an answer to the dilemma. Thus, a reaction mixture consisting of α-angelicalactone and benzophenone dissolved in excess thiophene was irradiated for 3 hours with uv light. At the end of the experiment two cyrstalline compounds were isolated in excellent yield. Structure elucidation of these compounds revealed that no [2 + 2] cycloaddition product between α-angelicalactone and thiophene was formed. Instead, the two crystalline compounds were isomeric oxetanes I and II.
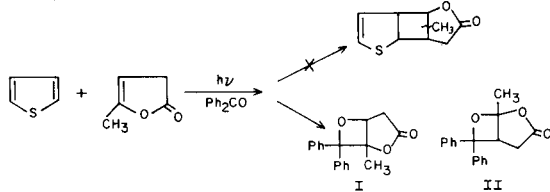

Fig. 1.

Product I predominated and the ratio I to II was 3/2. α-angelicalactone may perhaps be considered for the purposes of the cycloaddition reaction as an enol ether and as such the cycloaddition may proceed through a biradical intermediate. Of the two possible biradical precursors of the obtained products, Ia is more stable then IIa and for that reason product I forms in larger quantity (3).
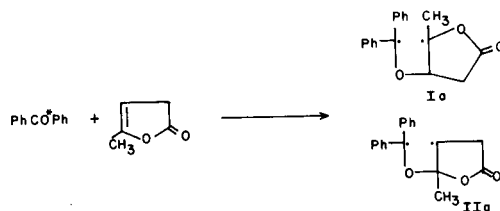

Fig. 2

The oxetanes were identified mainly by their [1]H-nmr, ^{13}C-nmr, ir as well as the mass spectra. Even though the [1]H-nmr spectra of the compounds may suffice to differentiate between the two isomers the ^{13}C-nmr spectrum is given as well and it also contributes to support the proposed structures.
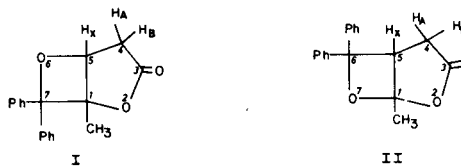

Fig. 3

In the [1]H-nmr spectrum aside from the resonances corresponding to the aromatic protons at about 7.40 ppm the characteristic features of the two spectra are as follows: a) the methyl proton resonances for II appear at 1.67 ppm while those for compound I appear slightly upfield at 1.33 ppm. On the other hand, the opposite may be observed for proton at C-5 which resonates at 5.13 ppm for I and shifts upfield to 3.91 ppm for II. This opposite effect on the positions of the methyl proton resonances in relation to that for the proton at C-5 for the two isomers should be expected, considering that the methyl group in II is located at a carbon atom between two oxygen atoms and proton at C-5 in I is located on a carbon atom next to an oxygen atom; in both cases a deshielding effect is operating on these groups. On the other hand, this effect is not present for proton a C-5 in II and may be attenuated for the methyl group in I since in this isomer it is located at a carbon atom next only to one oxygen atom. b) Proton at C-5

and the two protons at C-4 exhibit a typical ABX spectrum where proton at C-5 (X part) appears in both isomers as two doublets at 5.13 ppm for I and at 3.91 ppm for II as was explained above. On the other hand, the two protons at C-4 (AB part) give a complicated pattern made up of four doublets centered at 2.77 ppm for I and at 2.53 ppm for II. This resonance collapses in both cases to a typical AB spectrum (doublet of doublets) when decoupling of proton at C-5 is performed.

It is interesting to note that when compound II is left on the bench for several days at room temperature it slowly changes into a another compound. Since it was suspected that the compound was undergoing a thermal rearrangement a sample of it was sealed in a glass ampoule and heated in an oil bath for 20 minutes above its melting point. After cooling and opening the ampoule it is found, upon structure elucidation of the compound, that II rearranges quantitatively into compound III. The nmr spectrum of this isomer is virtually the same as that of compound II except for the fact that proton X (ABX spectrum) is slightly shifted downfield for III as compared to
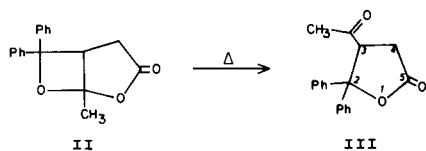

Fig. 4

the same proton in II. This result should be expected because that particular proton in II is under the anisotropic influence of the carbonyl group in the aliphatic sidechain: no deshielding influence of the sort is present in the neighborhood of the analogous proton in II. An interesting observation which calls one's attention when comparing the two spectra is the fact that the AB part of the ABX spectrum of III apears approximately as the mirror image of its counterpart in II. Perhaps, the explanation for this fact lies in the magnitude of the different coupling constants involved. Thus, J_{AB} is approximately the same for both compounds but J_{AX} in III is virtually the same as J_{BX} in II and likewise J_{AX} in II is approximately of the same order of magnitude as J_{BX} in III, as may be verified in Table I. Nevertheless, the most striking difference between the two compounds is found in the ir and the ^{13}C-nmr spectra. The ir spectrum of II exhibits only one carbonyl stretching absorption band at 1795 cm^{-1} while compound III shows two carbonyl absorption bands one at 1780 cm^{-1} corresponding to a lactone and a second band at 1725 cm^{-1} which may be correctly assigned to the aliphatic carbonyl group.

On the other hand, the ^{13}C-nmr spectrum of II shows only one carbonyl carbon atom resonance at 175.3 ppm while
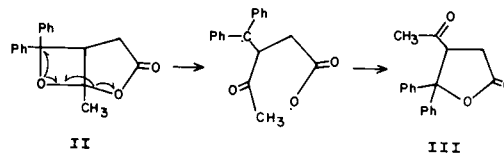
Table 1

NMR Data

Compound	Protons	Chemical shift (ppm)	Integral and multiplicity	Coupling constants (Hz)
I	1-CH$_3$	1.33	3 s	
	C-4	2.77	2 m	$J_{AB} = 19.0$
	C-5	5.13	1 d, d	$J_{AX} = 1.9$, $J_{BX} = 4.4$
II	1-CH$_3$	1.67	3 s	
	C-4	2.53	2 m	$J_{AB} = 19.1$
	C-5	3.91	1 d, d	
III	CH$_3$	1.68	3 s	$J_{AX} = 9.1$, $J_{BX} = 2.7$
	C-4	2.70	2 m	$J_{AB} = 17.7$
	C-3	4.30	1 d, d	$J_{AX} = 2.7$, $J_{BX} = 7.2$

The chemical shift for the aromatic protons was found at 7.4 ppm s, singlet; d, doublet; m, multiplet; deuteriochloroform TMS.

compound III exhibits two carbonyl carbon atom resonances at 206.3 and at 174.3 ppm which may be assigned to the aliphatic carbonyl group and to the lactone carbonyl group, respectively. The formation of compound III from II may presumably follow a pathway as illustrated in scheme I.

SCHEME I

It is important to note that this rearrangements is not induced by light. Compound I is far more stable than compound II upon standing and when it is subject to heating under the same experimental conditions used for II neither rearrangement nor decomposition product is isolated.
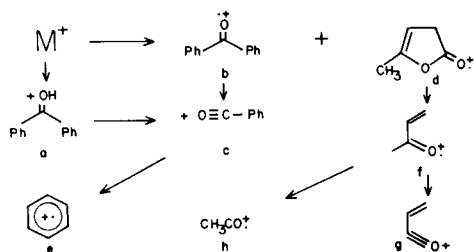
Table II

^{13}C-NMR Data

Carbon Atoms
C_n, ppm

Compound	CH$_3$	C-1	C-2	C-3	C-4	C-5	C-6	C-7
I	18.4 (q)	90.8 (s)	—	178.0 (s)	35.8 (t)	80.1 (d)	—	96.5 (s)
II	23.8 (q)	111.0 (s)	—	175.3 (s)	32.1 (t)	48.1 (d)	85.7 (s)	—
III	30.3 (q)	—	90.4 (s)	56.0 (d)	39.0 (t)	174.3 (s)	206.3 (s)	—

All the aromatic resonances were found between 125 and 145 ppm. All the spectra were measured in deuteriochloroform (TMS). Letters in parentheses give off-resonance ^{1}H information s,d,t and q for singlet, doublet, triplet and quartet, respectively.

The results of this investigation show that the thermal behavior of the two isomeric oxetanes obtained from α-angelicalactone is different from that of the oxetanes previously obtained in this laboratory from other five-membered ring heterocycles (4) in the sence that they do not undergo decomposition to yield the starting materials; instead, one rearranges and the other remains reasonably stable.

Inspection of the mass spectra of compounds I and II indicates that the retro Diels Alder type mechanism leading to the starting materials, benzophenone and α-angelica-lactone is an important fragmentation pathway. However, other fragmentation pathways appear to be important as well, as rationalized in scheme II (see Table III).

SCHEME II

Table III

Mass Spectral Data (a) m/e/%

Compound	M	a	b	c	d	e	f	q	h
	280	183	182	105	98	77	70	55	43
I	—	100	14	98	38	46	16	27	23
II	0.2	68	8	92	41	68	17	47	100
III	1	100	10	93	25	38	11	25	34

(a) The mass fragments in the table refer to Scheme II.

Table IV

Physical Data

Compound	Mp °C	Yield %	Empirical formula	Analysis Calcd./Found C	H
I	154-156	59	$C_{18}H_{16}O_3$	77.12	5.75
				77.10	5.79
II	151-152	36	$C_{18}H_{16}O_3$	77.12	5.75
				76.86	5.77
III	141-143	100	$C_{18}H_{16}O_3$	77.12	5.75
				77.18	5.79

1-Methyl-7,7-diphenyl-2,6-dioxabicyclo[3.4.0]heptan-3-one (I) and 1-Methyl-6,6-diphenyl-2,7-dioxabicyclo[3.2.0]heptan-3-one (II) (5).

α-Angelicalactone 6 g (0.06 mole) and benzophenone 7.2 g (0.04 mole) were dissolved in a mixture of hexane (230 ml) and methylene chloride (20 ml) and irradiated for 14 hours at -10° with a Hanovia 450 W mercury lamp in a quartz apparatus with a pyrex filter sleeve. Nitrogen was bubbled through the solution before and during irradiation. At the end of the irradiation the solvent was distilled under vacuum and the residue washed with benzene. The crude product was chromatographed over silica gel; two crystalline compounds were isolated from the chromatography column, product I (mp 154-156°) and product II (mp 151-152°) in 59 and 36% yield respectively.

2,2-Diphenyl-3-acetylbutyrolactone III.

Ten mg of II was placed in a pyrex ampoule and imersed in an oil bath at 140°. After 20 minutes heating the ampoule was removed from the bath and allowed to cool to room temperature. It was then opened and compound III removed, mp 141-143°, 100% yield.

REFERENCES AND NOTES

(1) G. O. Schenck, W. Hartmann and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963); C. Rivas, S. Krestonosich, E. Payo and L. Cortés, *Acta Cient. Venezolana*, **21**, 28 (1970); T. Nakano, C. Rivas, C. Pérez and K. Tori, *J. Chem. Soc., Perkin Trans.*, 2322 (1973).

(2) M. Ogata, H. Watanabe and H. Kano, *Tetrahedron Letters*, 533, (1967).

(3) N. J. Turro, "Modern Molecular Photochemistry", The Benjamin/Cummings Publishing Co. Inc., Menlo Park, CA, 1978, pp 437-438.

(4) R. A. Bolívar and C. Rivas, *Thermochim. Acta*, **12**, 353 (1975).

(5) The experiment with thiophene as the solvent is not reported because it did not react to form the [2 + 2] adduct and the purity of the crude product was improved using the mixture hexane-methylene chloride, instead of thiophene.