NOTES

Organic Photochemical Reactions. IV. Photoaddition Reactions of Various Carbonyl Compounds to Furan[1]

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In an earlier paper dealing with the photoaddition of propionaldehyde or benzaldehyde to furan,[2] it was shown that this addition gives oxetanes (Ia, Ib) without the ketones which are formed by the addition of acyl radical to olefins. The present investigation was undertaken to extend this photoaddition to some aliphatic and alicyclic aldehydes, unsaturated aldehydes and several ketones.

In these experiments, ultraviolet light from a 350 W. high pressure mercury lamp was used. A mixture of the carbonyl compound and furan was placed in a 180-ml. reaction vessel and irradiated at 5—10°C in a nitrogen atmosphere[3]: the reaction product was then isolated by distillation under reduced pressure.

The reaction conditions and the yields of the products are summarized in Table I.

The distilled fraction in each case was identified as an oxethane on the basis of an elementary analysis, a molecular weight determination, and a study of the infrared and NMR spectra.[4]

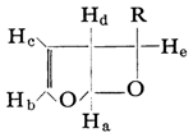
These oxetanes showed a strong band in the infrared region near 980 cm^{-1}, and no absorption

Table I. The reaction conditions and yield of the products

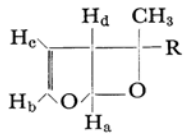
Carbonyl compound used g. (mole)	Furan used g. (mole)	Irrad. time hr.	Product: Oxetane g.	Product: Residue g.
CH_3CHO 22(0.5)	136(2)	6	8.3	2.2
C_2H_5CHO 28(0.48)	126(1.85)	6	10.0	2.5
n-C_3H_7CHO 28.8(0.4)	109(1.6)	6	15.5	3.7
i-C_3H_7CHO 24(0.33)	136(2)	6	8.5	2.0
n-$C_5H_{11}CHO$ 33(0.33)	136(2)	6	10.7	2.1
n-$C_6H_{13}CHO$ 38(0.33)	136(2)	6	11.7	1.8
 -CHO 37.3(0.33)	109(1.6)	6	16.1	3.5
C_6H_5CHO 42.5(0.4)	112(1.65)	6	24.5	3.5
 CHO 15	160	10	4.2	1.5
CH_2=$CHCHO$ 10	150	9	2.5	2.2
CH_3CH=$CHCHO$ 10.5	136	10	2.3	1.7
CH_3COCH_3 29(0.5)	136(2)	6	1.1	1.4
$C_2H_5COCH_3$ 36(0.5)	136(2)	6	0.8	1.3
$C_6H_5COCH_3$ 48(0.4)	109(1.6)	6	0.7	0.3

1) Presented at Symposium on the Organic Radical Synthesis, Osaka, September, 1964.
Part III: Y. Sasajima, K. Shima and H. Sakurai, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), in press.
2) S. Toki, K. Shima and H. Sakurai, This Bulletin, **38**, 760 (1965).
3) For the reaction apparatus, cf K. Shima, Y. Shigemitsu and S. Tsutsumi, ibid., **35**, 1728 (1962).
4) For an interpretation of the NMR spectra, see Ref. 2.

TABLE II. NMR SPECTRAL DATA*



Compound		τ-Value	Multiplicity	Coupling constant c.p.s.
Ic	a	3.72	Doublet	J_{ab} 1.0
R=CH_3	b	3.40	Quartet	J_{ad} 4.3
	c	4.67	Triplet	J_{bc} 2.9
	d	6.51	Multiplet	J_{bd} 1.0
	e	5.31	Octet	J_{cd} 2.9
				J_{de} 3.1
Id	a	3.75	Quartet	J_{ab} 0.9
R=n-C_3H_7	b	3.41	Quartet	J_{ad} 4.3
	c	4.70	Triplet	J_{bc} 2.9
	d	6.59	Multiplet	J_{bd} 0.9
	e	5.47	Sextet	J_{cd} 2.9
				J_{de} 3.1
Ie	a	3.76	Doublet	J_{ab} 0.9
R=i-C_3H_7	b	3.37	Quartet	J_{ab} 4.2
	c	4.70	Triplet	J_{bc} 3.0
	d	6.53	Multiplet	J_{bd} 0.9
	e	5.77	Quartet	J_{cd} 3.0
				J_{de} 3.0
If	a	3.73	Quartet	J_{ab} 0.9
R=n-C_5H_{11}	b	3.41	Quartet	J_{ad} 4.2
	c	4.70	Triplet	J_{bc} 3.0
	d	6.59	Multiplet	J_{bd} 0.9
	e	5.48	Sextet	J_{cd} 3.0
				J_{de} 3.0
Ig	a	3.73	Quartet	J_{ab} 1.0
R=n-C_6H_{13}	b	3.40	Quartet	J_{ad} 4.2
	c	4.69	Triplet	J_{bc} 3.0
	d	6.59	Multiplet	J_{bd} 1.0
	e	5.48	Sextet	J_{cd} 3.0
				J_{de} 3.0
Ih	a	3.92	Doublet	J_{ad} 4.1
	b	3.49	Doublet	J_{bc} 3.0
R= 	c	4.82	Triplet	J_{cd} 3.0
	d	6.59	Multiplet	J_{de} 3.0
	e	5.89	Quartet	
Ii	a	3.48	Doublet	J_{ab} 0.9
	b	3.33	Quartet	J_{ad} 4.2
R= 	c	4.60	Triplet	J_{bc} 2.8
	d	6.06	Multiplet	J_{bd} 0.9
	e	4.60	Doublet	J_{cd} 2.8
				J_{de} 3.2

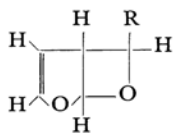


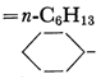
Compound		τ-Value	Multiplicity	Coupling constant c.p.s.
IIb	a	3.83	Doublet	J_{ab} 1.0
R=CH_3	b	3.42	Quartet	J_{ad} 4.2
	c	4.87	Triplet	J_{bc} 3.0
	d	6.46	Multiplet	J_{bd} 1.0
				J_{cd} 3.0
IIc**	a	3.83	Triplet	
R=C_2H_5	b	3.42	Quartet	
	c	4.89	Sextet	
	d	6.48	Multiplet	
IId	a	3.79	Doublet	J_{ab} 1.0
R=C_6H_5	b	3.31	Quartet	J_{ad} 4.2
	c	4.70	Triplet	J_{bc} 3.0
	d	6.18	Multiplet	J_{bd} 1.0
				J_{cd} 3.0

* Spectra were obtained on a Varian A-60 spectrometer using chloroform-d as solvent and tetramethylsilane as internal standard.

** NMR spectrum of this oxetane are different from others. The reason why proton a shows triplet (J=3.8 c.p.s.) and proton c shows triple-doublet (J=3.0 and 1.4 c.p.s.) are not clear.

of carbonyl or hydroxy groups was observed. The NMR spectral data are compiled in Table II.



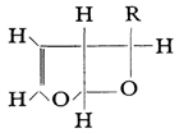
Ia R=C_2H_5
b C_6H_5
c CH_3
d n-C_3H_7
e i-C_3H_7
f n-C_5H_{11}
g R=n-C_6H_{13}
h 
i 
j CH_2=CH-
k CH_3CH=CH-

In the photoreaction of various aliphatic, alicyclic and unsaturated aldehydes with furan, oxetanes (Ic—Ik) were obtained. However, although in the case of n-butyraldehyde, acrolein and crotonaldehyde with furan, the main product was an oxetane, this fraction could not be purified by distillation. The properties of the oxetanes are shown in Table III.

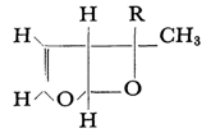
Recently, Schenck et al.[5] reported that, in the photoreaction of dimethylmaleic anhydride with furan in the presence of benzophenone as a sensitizer,

5) G. O. Schenck, W. Hartmann and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963).

TABLE III. THE PROPERTIES OF OXETANES



(I)

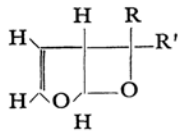


(II)

	b. p.	n_D	Anal.* C %	Anal.* H %
Ic, R=CH_3	41—42°C (11 mmHg)	1.4518 (20°C)	63.90 (64.27)	7.15 (7.19)
Ia, R=C_2H_5	74—75°C (30 mmHg)	1.4567 (20°C)	66.29 (66.64)	8.29 (7.99)
Id, R=n-C_3H_7	74—75°C (12 mmHg)	1.4518 (20°C)	70.38 (68.54)	9.02 (8.63)
Ie, R=i-C_3H_7	65—67°C (10 mmHg)		67.79 (68.54)	8.81 (8.63)
If, R=n-C_5H_{11}	106—108°C (12 mmHg)	1.4551 (20°C)	70.88 (71.39)	9.53 (9.59)
Ig, R=n-C_6H_{13}	81—82°C (1.5 mmHg)	1.4558 (20°C)	72.48 (72.49)	9.92 (9.96)
Ih, R=c-C_6H_{11}	86—87°C** (2 mmHg)		73.50 (73.30)	8.92 (8.95)
Ib, R=C_6H_5	104—105°C*** (1.2 mmHg)		76.12 (75.84)	6.02 (5.79)
Ii, R=C_4H_3O	80—83°C (1 mmHg)	1.5203 (16°C)	65.72 (65.85)	4.96 (4.91)
Ij, R=CH_2=CH	65—66°C (21 mmHg)	1.4728 (22.5°C)	66.28 (67.73)	6.62 (6.50)
Ik, R=CH_3CH=CH	86—90°C (17 mmHg)		68.27 (69.54)	7.21 (7.30)
IIb, R=CH_3	77—78°C (35 mmHg)	1.4510 (16.5°C)	66.64 (66.64)	8.20 (7.99)
IIc, R=C_2H_5	72—74°C (14 mmHg)	1.4552 (20°C)	68.67 (68.54)	8.77 (8.63)
IId, R=C_6H_5	86—87°C (1 mmHg)	1.5449 (11°C)	76.58 (76.57)	6.66 (6.43)

* The calculated values are in parentheses. ** m. p. 30°C. *** m. p. 49—50°C.

the oxetane (IIa) are formed. This structure was confirmed on the basis of its NMR spectrum by Gagnaire et al.[6] The photoreactions of acetone, methyl ethyl ketone and acetophenone with furan were undertaken to determine if these ketones would add to furan much as aldehydes adds to furan. It was observed that, in these photoreactions, the corresponding oxetanes (IIb—IId) are formed, but the yields of the oxetanes are very low compared with that of aldehydes to furan. It is interesting



IIa R=R′=C_6H_5
b R=R′=CH_3
c R=CH_3, R′=C_2H_5
d R=CH_3, R′=C_6H_5

that there is a very large difference in the oxetane yield between benzaldehyde and acetophenone. Yang et al.[7] pointed out that, in the photoaddition reactions of benzaldehyde, acetophenone and benzophenone to 2-methyl-2-butene, the low-lying triplet states of these carbonyl compounds are $n\rightarrow\pi^*$ in nature, that they are the reactive species in these reactions, and that the quantum yield of the oxetane formation from benzaldehyde is 0.45, and 0.1, from acetophenone. However, they did not discuss the difference in the oxetane yield. Our results are comparable with theirs. We are now studying the reaction mechanism in order to clarify the reason why there is a difference in oxetane yield.

The authors with to thank Dr. Angelo A. Lamola (University of Notre Dame) for his helpful discussions.

6) D. Gagnaire and E. Payo-Subiza, *Bull. Soc. Chim. France,* **1963**, 2623.

7) N. C. Yang, M. Nussim, M. J. Jorgenson and S. Murov, *Tetrahedron Letters,* **1964**, 3657.