Organic Photochemical Reactions. I. The Synthesis of Substituted Oxetanes by the Photoaddition of Aldehydes to Furans[1]

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Photochemical reactions of carbonyl compounds with olefins have been studied by many workers in recent years.[2] On the photoaddition of aldehydes to olefins, acyl addition affording ketones, direct addition yielding oxetanes, and allylic addition giving unsaturated carbinols have been observed. However, little attention has been paid to the addition of aldehydes to conjugated olefins. In the present work, furan and 2-methylfuran were chosen as the conjugated olefins without an activated allylic hydrogen atom. It seemed that it would be interesting to investigate what type of reaction occurs between aldehydes (propionaldehyde and benzaldehyde) and furans on irradiation.

In this experiment, an ultraviolet light from a 350 W. high pressure mercury lamp was used. A mixture of aldehyde and furan (mole ratio: ca. 1 : 4) was irradiated in a nitrogen atmosphere at 5—10°C for 6 hr., and then the reaction product was isolated by distillation under reduced pressure.

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

The distilled fraction in each case was identified as an oxetane from the following observations. In the photochemical reaction of propionaldehyde and furan, a fraction with a b. p. of 74—75°C (30 mmHg) was obtained. This fraction was decomposed into its starting materials (mole ratio: 1 : 1) when passed through a Dinonyl Phthalate and Silicone DC 550 column at 80°C. This fraction was confirmed to be a 1 : 1 adduct on the basis of the above finding, elementary analysis and molecular weight determination. The infrared spectrum showed the presence of a vinyl ether group[3] and a trimethylene oxide ring,[3] but the absorptions of a carbonyl group and a hydroxy group were not observed. The structure of this photoadduct, therefore, is either Ia or Ib.

This was determined by means of the NMR spectrum. NMR spectral data are compiled

TABLE I. THE REACTION CONDITIONS AND YIELD OF THE PRODUCTS

Furan g.	Aldehyde g.	Oxetane g.	Residue g.	Yield[a] %	Ultimate yield[b] %
C_4H_4O 126	C_2H_5CHO 28	10	2.5	17	80
C_4H_4O 112	C_6H_5CHO 42.5	24.5	3.5	35	88
CH_3-C_4H_3O 125	C_2H_5CHO 23.2	9.5	3.5	17	73
CH_3-C_4H_3O 120	C_6H_5CHO 38.5	22	3.4	32	87

a) Yield of products based on aldehyde used.
b) Yield of products based on aldehyde consumed.

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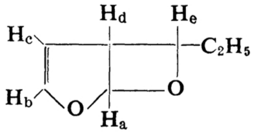
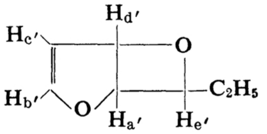
[1] Reported at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[2] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949); G. Büchi, C. G. Inman and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954); P. de Mayo, J. B. Stothers and W. Templeton, *Proc. Chem. Soc.*, **1960**, 72; *Can. J. Chem.*, **39**, 488 (1961).

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London (1958), pp. 117, 119.



(Ia)

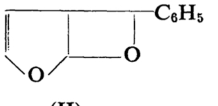


(Ib)

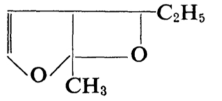
in Table II. Supposing that it is Ib, as all protons except for ethyl protons are adjacent to oxygen or are vinylic, it may be expected that the τ-value of each proton will be less than 5.5. However, a proton with a τ-value of 6.58 was observed. Moreover, although a proton a′ would be a triplet and a proton d′ would be a sextet or octet in the structure Ib, a doublet and a complex multiplet were actually observed. The structure, therefore, was identified as 6-ethyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (Ia). The infrared spectrum of the residue showed strong bands of the carbonyl and hydroxy groups. The ratio of the residue to Ia increased with the irradiation time. Ia was rather stable in a sealed tube. When Ia was exposed to air, however, its infrared spectrum gradually became similar to that of the residue. The residue, therefore, seems to consist of the products formed from Ia by further reaction by, for instance, light or oxygen.

In the photochemical reaction of benzaldehyde and furan, the photoadduct was similarly identified as 6-phenyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (II).

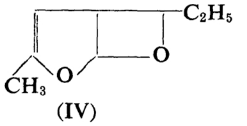
In the case of propionaldehyde (or benzaldehyde) and 2-methylfuran, mixtures of III (or V) and IV (or VI) were obtained.



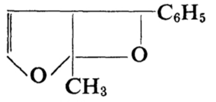
(II)



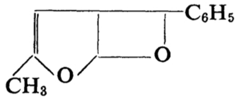
(III)



(IV)

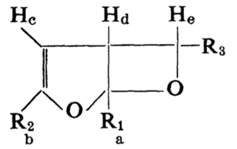


(V)



(VI)

TABLE II. NMR SPECTRAL DATA*

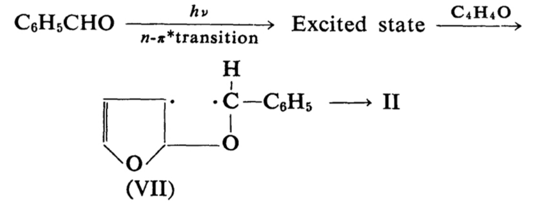


Compound		τ-Value	Multiplicity	Coupling const., c.p.s.
Ia	a	3.73	Quartet	J_{ab} 0.9
R_1=H	b	3.40	Quartet	J_{ad} 4.4
R_2=H	c	4.70	Triplet	J_{bc} 2.8
R_3=C_2H_5	d	6.58	Multiplet	J_{bd} 0.9
	e	5.53	Sextet	J_{cd} 2.8
				J_{de} 2.8
II	a	3.53	Doublet	J_{ab} 0.8
R_1=H	b	3.37	Quartet	J_{ad} 4.4
R_2=H	c	4.62	Triplet	J_{bc} 2.9
R_3=C_6H_5	d	6.43	Multiplet	J_{bd} 0.8
	e	4.50	Doublet	J_{cd} 2.9
				J_{de} 2.9
III**	a	8.38	Singlet	J_{bc} 3.1
R_1=CH_3	b	3.49	Quartet	J_{bd} 1.0
R_2=H	c	4.78	Triplet	J_{cd} 3.1
R_3=C_2H_5	d	6.89	Sextet	J_{de} 3.1
	e	5.71	Sextet	
IV**	a	3.80	Doublet	J_{ad} 4.0
R_1=H	b	8.10	Triplet	J_{bc} 1.3
R_2=CH_3	c	5.09	Sextet	J_{bd} 1.3
R_3=C_2H_5	d	6.63	Multiplet	J_{cd} 2.7
	e	5.71	Sextet	J_{de} 3.2
V**	a	8.30	Singlet	J_{bc} 3.1
R_1=CH_3	b	3.38	Quartet	J_{bd} 0.9
R_2=H	c	4.62	Triplet	J_{cd} 3.2
R_3=C_6H_5	d	6.60	Sextet	J_{de} 3.2
	e	4.48	Doublet	
VI**	a	3.53	Doublet	J_{ad} 4.6
R_1=H	b	8.04	Triplet	J_{bc} 1.2
R_2=CH_3	c	4.93	Multiplet	J_{bd} 1.2
R_3=C_6H_5	d	6.42	Multiplet	J_{cd} 3.2
	e	4.48	Doublet	J_{de} 3.2

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

** Data of III and IV, V and VI were obtained from the spectrum of products mixture, respectively.

The reaction paths for the formation of oxetanes are probably similar in all cases. As a typical example, the reaction of benzaldehyde with furan probably proceeds by the following path.



$$C_6H_5CHO \xrightarrow[n\text{-}\pi^*\text{transition}]{h\nu} \text{Excited state} \xrightarrow{C_4H_4O}$$

$$\cdot\overset{H}{C}-C_6H_5 \longrightarrow \text{II}$$

(VII)

The intermediate (VII) has the structure which is to be expected from the principle of the maximum resonance stabilization of the intermediate diradical. VII is also expected from the simple LCAO-MO. Since the excited benzaldehyde has a free radical character[4] at

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[4] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

the oxygen atom, as is to be expected from an excitation of the n-π^* type, the oxygen atom with a free radical character will attack the site of higher free valence or a more frontier electron density5) of the furan ring to yield VII.

Experimental6)

Materials.—Propionaldehyde was purified by distillation; b. p. 50°C, n_D^{20} 1.3689. Benzaldehyde was also purified by distillation; b. p. 36.5°C (2 mmHg), n_D^{20} 1.5444. Furan7) was prepared by the decarboxylation of 2-furancarboxylic acid, formed by the Cannizzaro reaction of furfural, and purified by fractional distillation over calcium chloride; b. p. 31.5°C. 2-Methylfuran8) was prepared by the following method. A mixture of 270 g. of furfural and 300 g. of a 30—40% aqueous hydrazine solution was added drop by drop to 50 g. of potassium hydroxide in a 1-l. Claisen flask, which was then placed in an oil bath heated at 150—160°C. The distillate was collected, and the upper layer was separated, dried over potassium hydroxide and distilled; b. p. 63°C. These materials were gas chromatographically pure and were redistilled before use.

6-Ethyl-2,7-dioxa-bicyclo-[3,2,0]-Δ^3-heptene (Ia).—A mixture of 126 g. (1.85 mol.) of furan and 28 g. (0.48 mol.) of propionaldehyde was placed in a 180 ml. reaction vessel and irradiated at 5—10°C in a nitrogen atmosphere for 6 hr.9) The unreacted materials were then distilled off, and the portion boiling at 70—75°C (30 mmHg) was collected; yield, 10 g. (17%). This fraction was redistilled at 30 mmHg (b. p. 74—75°C); n_D^{20} 1.4567. Principal infrared bands: 3075, 2945, 1605, 1460, 1213, 1198, 1130, 1043, 1013, 985, 950, 887, 850 and 715 cm^{-1}.

Found: C, 66.29; H, 8.29; mol. wt., 127. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99%; mol. wt., 126.

6-Phenyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (II).—A mixture of 112 g. (1.65 mol.) of furan and 42.5 g. (0.40 mol.) of benzaldehyde was irradiated at 5—10°C for 6 hr. and then treated in the same manner as has been discribed above. A 100—115°C (2 mmHg) fraction was then collected; yield, 24.5 g. (35%). This fraction was redistilled at 1.2 mmHg (b.p. 104—105°C); m.p. 49—50°C. Principal infrared bands: 3080, 2940, 1608, 1458, 1380, 1198, 1130, 1040, 940 and 708 cm^{-1}.

Found: C, 76.12; H, 6.02; mol. wt., 175. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%; mol. wt., 174.

1-Methyl-6-ethyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (III) and 3-Methyl-6-ethyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (IV).—A mixture of 125 g. (1.52 mol.) of 2-methylfuran and 23.2 g. (0.40 mol.) of propionaldehyde was irradiated and then treated in the same manner as has been described above. A 60—90°C (17 mmHg) fraction was collected; yield, 9.5 g. (17%). This fraction was redistilled at 15 mmHg (b. p. 65—68°C), n_D^{20} 1.4473. Principal infrared bands: 3060, 2910, 1668, 1605, 1460, 1382, 1222, 1167, 1125, 1050, 1010, 980, 955, 890, 850 and 720 cm^{-1}.

Found: C, 68.45; H, 8.65; mol. wt., 146. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63%; mol. wt., 140.

This fraction was identified by NMR spectra as being composed of III and IV.

1-Methyl-6-phenyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (V) and 3-Methyl-6-phenyl-2, 7-dioxa-bicyclo-[3, 2, 0]-Δ^3-heptene (VI).—A mixture of 120 g. (1.46 mol.) of 2-methylfuran and 38.5 g. (0.36 mol.) of benzaldehyde was irradiated and treated in the same manner as has been described above. A 90—110°C (1 mmHg) fraction was collected; yield, 22 g. (32%). This fraction was redistilled at 1 mmHg (b. p. 100—110°C), n_D^{20} 1.5380. Principal infrared bands: 3000, 2945, 1665, 1605, 1490, 1383, 1350, 1224, 1162, 1103, 1040, 950, 890, 750 and 698 cm^{-1}.

Found: C, 76.60; H, 6.63; mol. wt., 186. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%; mol. wt., 188.

This fraction was identified by NMR spectra as being composed of V and VI.

Summary

The photochemical reaction of aldehydes (propionaldehyde and benzaldehyde) and furan have been studied in the liquid phase; two new compounds, oxetanes I and II have easily been produced with a high purity by this photo-reaction.

In the case of 2-methylfuran and propionaldehyde (or benzaldehyde), a mixture of oxetanes III and IV (or V and VI) has also been obtained.

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5) S. Nagakura and T. Hosoya, This Bulletin, 25, 179 (1952).

6) The boiling and melting points are uncorrected. The molecular weights of the samples were determined by the cryoscopic method in benzene.

7) W. C. Wilson, "Organic Syntheses," Coll. Vol. I, 274, 276 (1956).

8) S. Okumura, "Zikken Yūki Kagaku (Experimental Organic Chemistry)", Kyōritsu Shuppan, Tokyo (1953), p. 107.

9) Reaction apparatus: K. Shima, Y. Shigemitsu and S. Tsutsumi, This Bulletin, 35, 1728 (1962).