Photoaddition of Carbonyl Compounds to Five-Membered Ring Heterocycles

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It has been possible to prepare oxetanes from several carbonyl compounds and derivatives of furan, pyrrole and thiophene. This account summarizes the successful and some of the unsuccessful attempts carried out in this laboratory to extend the Paterno-Büchi reaction to the common five-membered heterocyclic systems; the new compounds obtained in this connection are reported and several interesting facts which may help understand the reactivity of heterocycles in the presence of excited carbonyl compounds are commented.

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Introduction.

Some years ago, after the first series of oxetanes, from methylfurans and benzophenone (1) was synthesized in this laboratory, the goal was to study the scope and limitations of the carbonyl photoadditions to the common five-membered heterocycles. Oxetanes from pyrrole and thiophene were not known at that time. The experience acquired in the reaction studied will be useful to extend the Paterno-Büchi reaction to other five-membered ring heterocycles.

Results.

The direct [2 + 2] photoaddition of benzophenone to furan was first achieved independently by two groups of workers (2,3). The product was later unequivocally identified by nmr as the 6,6-diphenyl-2,7-dioxabicyclo[3.2.0]-Δ^3-heptane.

Since the reaction seemed to be potentially useful it was decided to investigate its synthetic utility. Thus, irradiation of benzophenone in 2- and 3-methylfuran, 2,4- and 2,3-dimethylfuran and 2-furfuryl alcohol afforded oxetanes in excellent yield (1,5). More recently, using furan and 2-methylfuran as the substrates the reaction was carried out with other carbonyl compounds such as 4-methyl, 4-methoxy and 4-chlorobenzophenone and 2-benzoylthiophene; 1- and 2-naphthaldehyde were also irradiated but only in the presence of furan. All of these carbonyl compounds give oxetanes in good yield. The products were identified by their nmr and mass spectral analysis (1,5).

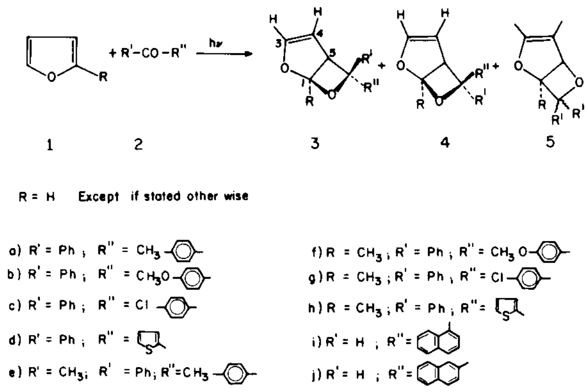


Fig._ 1

On the other hand in an earlier communication (6) dealing with an investigation on the sensitized photoaddition of methylmaleic anhydrides to several thiophene derivatives it was found that when the reaction was carried out in 2,5-dimethylthiophene, the benzophenone used as the sensitizer added to the heterocycle to form an oxetane. The reaction was later carried out with the following carbonyl compounds: 1- and 2-naphthaldehyde, benzaldehyde, 2-, 3- and 4-benzoylpyridine and 2-benzoylthiophene. Except for 2-naphthaldehyde and benzaldehyde all of these compounds formed the corresponding oxetanes with 2,5-dimethylthiophene as reported before (7).

In an attempt to make the reaction more general and to try to answer some questions about the isomer composition observed in the latter series of compounds, irradiations of 4-methyl, 4-methoxy and 4-chlorobenzophenone, 1,1-dinaphthyl and 2,2'-dipyridylketone were carried out in the presence of 2,5-dimethylthiophene. Some of the reactions gave the expected products while others gave products that were rather unexpected.

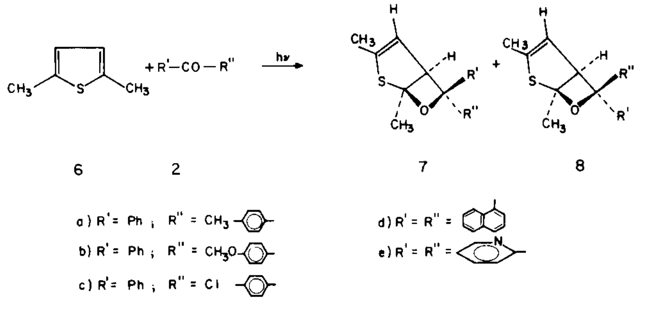


Fig._ 2

The stereochemistry depicted for the oxetanes is supported by NOE studies (8).

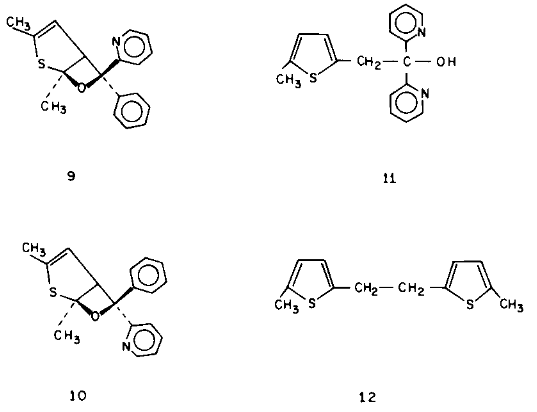


Fig _3

In the pyrrole series, pyrrole, 1-methyl, 1-phenyl, 2,5-dimethyl, 1-benzyl, 1-benzoyl, 1-acetyl, 1-benzenesulphonyl and 1-carbomethoxypyrrole were tested as substrates with excited benzophenone. Out of all of these, 1-benzoylpyrrole was the only one that yielded an oxetane (a double oxetane from addition of two benzophenone molecules one to each double bond in the ring).

These and other results obtained in the pyrrole series have already appeared elsewhere (9).

Discussion.

As is well known, the aromaticity of the common five-membered heterocycles increases in the following order: furan, pyrrole and thiophene (10). As one would expect, furan behaves throughout all these photoaddition reactions as a conjugated system of two double bonds reacting smoothly with benzophenone and other analogs to yield oxetanes. In the series of methyl-substituted furans and under the experimental conditions described below only addition to the double bond bearing the methyl substituent is observed for each furan derivative in the presence of each excited carbonyl compound (1). This fact contrasts with the mixture of isomeric oxetanes derived from addition of the carbonyl compound to each double bond in the ring observed by Toki, *et al* (11) in the photolysis of aldehydes such as benzaldehyde and acetaldehyde in the 2-methylfuran.

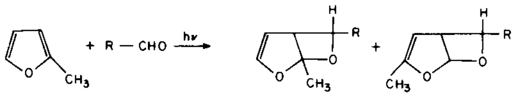


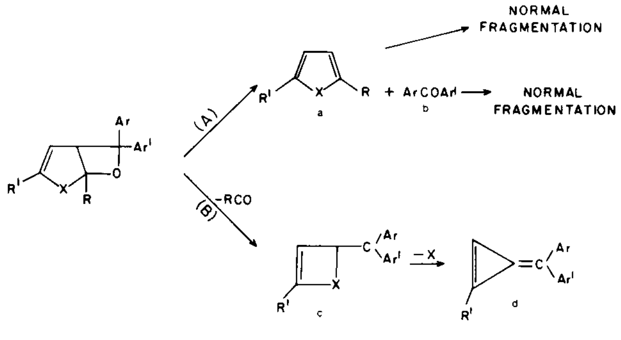
Fig _ 4

In the present investigation the only instances where mixtures of isomers were encountered occurred when unsymmetric carbonyl compounds such as 2-benzoylthiophene were irradiated in the presence of furan and 2-methylfuran. These mixtures consisted of two geometrical isomers of the type 3 and 4. The presence of two isomers is inferred from inspection of the nmr spectra.

The more different the two groups bonded to the carbonyl group, the more clearly the two isomers are detected; such is the case in the derivatives of the 2-benzoylthiophenes. When the two groups are very similar, as in the case of the substituted benzophenones, the presence of the two isomers is not so obvious.

Compound 5 has not been isolated in the 1:1 photochemical reactions between heterocyclic and carbonyl compounds. When Schenck first isolated the adduct of benzophenone and furan there was some ambiguity as to the position of the oxygen atom in the four membered ring. Later on by analogy to the positions of the proton signals in the nmr spectrum of trimethylene oxide an argument was devised so as to lead to the assignment of structure 4 to the simple oxetanes of furan (4).

Mass spectral analyses of the oxetanes (5) carried out in this laboratory have shown that in general in addition to a retro Diels-Alder type A, process (Scheme I) where one mass fragment corresponds to the heterocyclic and the other to the carbonyl moiety, fragmentation such as B is observed as well.



Scheme I

This is more clearly observed in the oxetanes derived from 2,5-dimethylthiophene (7). It is interesting to note that the thermal decomposition of the oxetanes as studied by differential scanning calorimetry follows the same type of retro Diels-Alder cleavage (12).

In addition to the above evidence, the results of NOE studies have confirmed, on a firmer basis, that the oxygen atom in the four-membered ring is next to the carbon adjacent to the hetero atom in the five-membered ring. Thus, enhancement in the intensities of the 5-H signals were clearly observed when second rf fields were applied to the appropriate position within the resonances of the phenyl proton signals (8).

As mentioned above, when carbonyl compounds unsymmetrically substituted on both sides of the carbonyl group are irradiated in furan, 2-methylfuran or in 2,5-dimethylthiophene mixtures of geometrical isomers 3 and 4 and 7 and 8 respectively are obtained.

Out of all the products from these heterocycles the mixture obtained from the reaction of 2-benzoylthiophene and furan probably serves to illustrate the presence of two compounds. The nmr spectrum exhibits, as was previously described (7) for derivatives of 2,5-dimethylthiophene two sets of identical signals for each non-aromatic proton. From the intensities of the peaks it may be inferred that the two isomers are formed in approximately equal proportions. In a previous paper (7) it was suggested by inspection of 100 MHz nmr spectrum of the oxetane derived from 2-benzoylpyridine and 2,5-dimethylthiophene, that the ratio of isomer 9 to 10 is 53.5/46.5. Even though they could not be separated by chromatographic methods, since the oxetane derived from benzophenone and 2,5-dimethylthiophene had been isolated in pure form, it seemed reasonable to prepare also the oxetane from 2,2′-dipyridylketone and this heterocycle in order to compare the three nmr spectra.

In the benzophenone oxetane the non-aromatic protons are under the anisotropic influence of the phenyl groups only, in the dipyridyl ketone derivative they are under the influence of only pyridyl groups; in the mixture of the two isomers (*e.g.* compounds **9** and **10**) each proton is under the influence of either group which is presumably the cause of the appearance of two identical signals for each proton only differentiated by the chemical shift. Comparing the three spectra one could perhaps assign each signal on a firmer basis. Unfortunately, the irradiation of 2,2′-dipyridyl ketone in 2,5-dimethylthiophene yielded alcohol **11** as the only product and no oxetane could be isolated.

The reaction between the 4-chloro and 4-methylbenzophenone and 2,5-dimethylthiophene yielded the corresponding mixtures of oxetanes and a liquid which from its spectral characteristics appears to be a dimer of 2,5-dimethylthiophene (**12**). On the other hand when 4-methoxybenzophenone was irradiated in 2,5-dimethylthiophene no oxetane was isolated. The only compound which was separated chromatographically was dimer **12**. Presumably the ketone abstracts a hydrogen atom from one of the methyl groups of 2,5-dimethylthiophene and two of these free radicals couple to yield the dimer.

1,1-Dinaphthyl ketone was irradiated in 2,5-dimethylthiophene in order to compare the nmr spectrum of the

Table I

NMR Spectral Data on the Furan Oxetanes

Oxetane	Protons	Chemical shift (ppm)	Integral and multiplicity		Coupling Constants (Hz)
3a	H_1	6.38	1	q	$J_{1,3} = 0.6$
4a	H_3	6.47	1	octet	$J_{1,5} = 4.2$
	H_4	4.98	1	t	$J_{4,3} = J_{4,5} = 3.0$
	H_5	4.42	1	heptet	$J_{3,5} = 1.3$
	Ph-CH_3	2.35 and 2.30	3, 3, s, s		
3b	H_1	6.33	1,	2 q	$J_{1,3} = 0.6$
4b	H_3	6.52	1	octet	$J_{1,5} = 4.2$
	H_4	4.97	1	2 t	$J_{4,3} = J_{4,5} = 3.0$
	H_5	4.40	1	heptet	$J_{5,3} = 1.3$
	Ph-CH_3	3.74 and 3.80	3, 3, s, s		
3d	H_1	6.48	1	d	$J_{1,3} = 0.8$
	H_3	6.33	1	q	$J_{1,5} = 4.4$
	H_4	4.85	1	t	$J_{3,4} = J_{4,5} = 3.0$
	H_5	4.40	1	m	
4d	H_1	6.19	1	d	$J_{1,3} = 0.8$
	H_3	6.55	1	q	$J_{1,5} = 4.4$
	H_4	5.02	1	t	$J_{3,4} = J_{4,5} = 3.0$
	H_5	4.25	1	m	
3i	H_1	6.45	1	2 t	$J_{1,5} = 4.8$
	H_3	6.80	1	2 t	$J_{1,3} = J_{1,6} = 0.8$
	H_4	5.68	1	t	$J_{3,4} = J_{4,5} = 3.0$
	H_5	3.50	1	m	$J_{5,6} = 3.3$
	H_6	6.15	1, d (broad)		
3j	H_1	6.57	1	2 t	$J_{1,3} = J_{1,6} = 1.0$
	H_3	6.72	1	2 t	$J_{1,5} = 3.4$
	H_4	5.50	1	t	$J_{3,4} = J_{4,5} = J_{5,6} = 3.0$
	H_5	3.68	1	m	
	H_6	5.60	1, d (broad)		

(a) The chemical shift for the aromatic protons in these compounds is found between 6.70 and 8.00 ppm (b) s, singlet: d, doublet: t, triplet: q, quartet.
(c) They correspond to each one of the two isomers mentioned in the discussion.

product with that of the product derived from 1-naphthaldehyde in an attempt to differentiate the two geometrical isomers which had presumably been formed as it had happened with other asymetrically substituted carbonyl compounds (7). However, 1,1-dinaphthyl ketone yielded only polymeric materials. On the other hand, ^{13}C studies on the oxetane derived from 1-naphthaldehyde and 2,5-dimethylthiophene unambiguously established the presence of only one isomer (13). It is possible that the presence of one naphthyl group, because of steric reasons, favors the formation of only one isomer and by the same token the presence of two naphthyl groups as it is the case with 1,1-dinaphthyl ketone totally prevents the formation of an oxetane; that may be the reason why only polymeric materials are formed in this case. The steric argument may be more reasonable to explain the behaviour of these carbonyl groups substituted with naphthyl groups rather than the purely photochemical argument based on the type of excitation involved (n, π^* versus π,π^*) since it has been shown that oxetanes may be formed even when π, π^* excitation predominates over n, π^* (14).

The fact that 2-benzoylthiophene reacts with hetero-

Table II

NMR Spectral Data on the 2-Methylfuranoxetanes

Oxetanes	Protons	Chemical shift (ppm)	Integral and multiplicity		Coupling Constants (Hz)
3e	1-CH_3	1.55	3	s	$J_{3,5}$ = 1.2
4e	H_3	6.33	1	q	$J_{3,4}$ = $J_{4,5}$ = 3.0
	H_4	4.86	1	t	
	H_5	4.12	1	q	
	Ph-CH_3	2.27 and 1.55	3, 3	s, s	
3f	1-CH_3	1.57	3	s	$J_{3,5}$ = 1.2
4f	H_3	6.45	1	q	$J_{3,4}$ = $J_{4,5}$ = 3.0
	H_4	4.92	1	t	
	H_5	4.15	1	q	
	Ph-OCH_3	3.77	3	s	
3g	1-CH_3	1.56	3	s	$J_{3,5}$ = 1.2
4g	H_3	6.42	1	q	$J_{3,4}$ = $J_{4,5}$ = 3.0
	H_4	4.85	1	t	
	H_5	4.17	1	q	
3h	1-CH_3	1.75	3	s	$J_{3,5}$ = 1.2
	H_3	6.56	1	q	$J_{3,4}$ = $J_{4,5}$ = 3.0
	H_4	4.97	1	t	
	H_5	4.07	1	q	
4h	1-CH_3	1.55	3	s	$J_{3,5}$ = 1.2
	H_3	6.33	1	q	$J_{3,4}$ = $J_{4,5}$ = 3.0
	H_4	4.78	1	t	
	H_5	4.18	1	q	

Table III

NMR Spectral Data on the 2,5-Dimethylthiophene Oxetanes and Non-Oxetan Compounds

Compound	Protons	Chemical shift (ppm)	Integral and multiplicity		Coupling Constants (Hz)
7a	Aromatic	7.33	9	m	
8a	1- and 3-CH_3	1.87	6,	s and t	$J_{4,3}$-CH_3 = 1.5
	H_4	4.83	1,	sextet	$J_{5,3}$-CH_3 = 1.5
	H_5	4.47	1,	sextet	$J_{4,5}$ = 2.8
	Ph-CH_3	2.29 and 2.37	3, 3,	s, s	
7c	Aromatic	7.36	9	m	
8c	1- and 3-CH_3	1.83	6,	s and t	$J_{4,3}$-CH_3 = 1.6
	H_4	4.90	1,	sextet	$J_{5,3}$-CH_3 = 1.6
	H_5	4.45	1,	sextet	$J_{4,5}$ = 3.2
11	Pyridilic + OH	7.00-8.60	9	m	
	2-CH_2-	3.83	2	s	
	H_3 and H_4	6.42	2	s	
	5-CH_3	2.27	3	s	
12	2- and 2'-CH_2	3.08	4	s	
	H_3' H_3', H_4' H_4'	6.58	4	s	
	5- and 5'-CH_3				

cyclic substrates to give oxetanes contrasts with the findings of other authors who have studied its photochemical behaviour in the presence of olefinic substrates. Cantrell (15) has found that irradiations of 2-benzoylthiophene in excess 2-butene results in [2 + 2] cycloaddition of the olefin to one of the double bonds in the thiophene ring as shown, (Fig. 5).

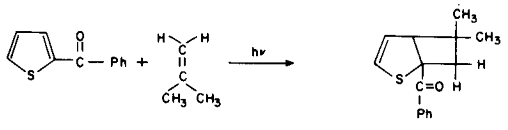


Fig._ 5

Table IV

Mass Spectral and Physical Data for the Oxetanes

Compound/Fragment	a	b	c	d	M⁺	mp °C	Yield %
3a/4a	68 (2)	196 (100)	235 (23)	218 (56)	264 (58)	97-100	37
3b/4b	68 (15)	212 (49)	251 (18)	234 (50)	280 (75)	98-101	98
3c/4c	68 (15)	216 (15)	—	—	284 (65)	140-141	50
3d/4d	68 (15)	188 (25)	—	—	256 (70)	96-98	80
3e/4e	82 (100)	196 (9)	235 (8)	218 (4)	278 (2)	128-130	12
3f/4f	82 (100)	212 (29)	251 (2)	—	294 (3)	98-102	15
3g/4g	82 (100)	216 (3)	255 (3)	—	298 (1)	162-163	15
3h/4h	82 (100)	188 (28)	227 (10)	210 (8)	270 (7)	120-122	20
3i	68 (45)	156 (100)	195 (20)	178 (14)	224 (13)	100-105	25
3j	68 (40)	156 (100)	195 (25)	178 (18)	224 (15)	74-76	15
7a/8a	112 (100)	196 (10)	265 (4.1)	232 (2)	308 (1)	94-96	27
7c/8c	112 (100)	216 (11)	285 (1.4)	252 (0.5)	328 (0.3)	128-130	57

a, b, c, d Refer to Scheme I.

Table V

Elemental Analysis for the Photoproducts

Compound	Formula	Calcd./Found			
		C	H	S	N
3, 4a	$C_{18}H_{16}O_2$	81.80	6.10	—	—
		81.41	6.04		
3, 4b	$C_{18}H_{16}O_3$	77.13	5.75	—	—
		77.08	5.78		
3, 4d	$C_{15}H_{12}O_2S$	70.29	4.69	12.50	—
		70.29	4.68	12.30	
3, 4e	$C_{19}H_{18}O_2$	81.99	6.52	—	—
		81.38	6.44		
3, 4f	$C_{19}H_{18}O_3$	77.51	6.16	—	—
		77.32	6.10		
3, 4g	$C_{18}H_{15}ClO_2$	72.37	5.06	—	—
		72.41	4.96		
3, 4h	$C_{16}H_{14}O_2S$	71.09	5.22	11.86	—
		71.00	5.16	11.70	
3i	$C_{15}H_{12}O_2$	80.34	5.39	—	—
		80.15	5.38		
7, 8a	$C_{20}H_{20}OS$	77.89	6.53	10.39	—
		78.02	6.33	10.09	
7, 8c	$C_{19}H_{17}ClOS$	69.40	5.21	9.75	—
		69.05	5.10	10.00	
11	$C_{17}H_{16}N_2OS$	68.89	5.45	10.83	9.46
		68.79	5.45	10.84	9.20

A satisfactory analysis for **3j** could not be obtained due to instability.

The explanation given for this behaviour is that the mode of excitation of 2-benzolthiophene is of the $\pi \rightarrow \pi^*$ type (15).

Thiophene and many of its derivatives undergo the type of [2 + 2] cycloaddition just mentioned (16). However, thus far the only thiophene derivative that undergoes oxetane formation is 2,5-dimethylthiophene. Several authors have speculated (17) that the inertness of thiophene towards this kind of reaction is due to its highly aromatic character. In this laboratory, thiophene, 2-methylthiophene and 3-methylthiophene have been tested as substrates with several excited carbonyl compounds with no success at all.

Since the triplet state of thiophene presumably lies at 69 Kcal/mole above its ground states (18), which is very similar to that of benzophenone (T_1 = 69 Kcal/mole), ketones with a higher triplet state such as propiophenone (T_1 = 74 Kcal/mole) were irradiated in thiophene. The reasoning behind these experiments was that perhaps a ketone with a higher triplet energy would be more effective in adding to the highly aromatic ring. However, the ketone was recovered quantitatively. The inertness of thiophene may be considered from another angle; thiophene may very well behave as a quencher of the triplet state of the ketones under consideration. From this standpoint several carbonyl compounds with very low lying triplet states were chosen; they were 1-naphthaldehyde, fluorenone and bibenzyl.

The irradiations of these compounds in thiophene gave only polymeric materials.

Since it is well known that 2-phenylthiophene rearranges under irradiation to 3-phenylthiophene (19) and it does not yield oxetane, this result suggested that perhaps 2-methylthiophene would undergo an analogous rearrangement that in addition to the quenching effect would compete with oxetane formation. In fact, 2-methylthiophene was irradiated and no reaction took place; however, when 3-methylthiophene is irradiated 2-methylthiophene is formed in about 2% yield as disclosed by following the reaction by gas chromatography. This reaction was carried out under the same conditions (pyrex filter ≥ 300 nm) used for the oxetane forming reactions. Kellog (20) found that 3-methylthiophene rearranges to 2-methylthiophene using light of shorter wavelength (254 nm) but when he tried the reverse reaction 3-methylthiophene yields decomposition products.

Since electron donating groups attached to a conjugated diene presumably raise its lower triplet energy level (14) one would be inclined to believe that one methyl group is not as effective as two methyl groups in raising it sufficiently in this type of compound to change it from a quencher into a substrate for the excited species to form a cycloaddition compound. Thus, it should be expected that 2- and 3-methylthiophene, like thiophene, are still good quenchers but 2,5-dimethylthiophene has its lowest triplet energy above that of the carbonyl compounds used in this investigation.

In order to generalize this reaction and to test the ideas stated in the previous paragraph thiophenes substituted with more than one methyl group were synthesized in this laboratory, and tested for oxetane formation. They were 2,3-dimethyl, 3,4-dimethyl and 2,3,5-trimethylthiophene; of all these compounds only 2,3-dimethylthiophene undergoes the oxetane forming reaction (21).

On the other hand quenching experiments with different thiophene derivatives are in hand in order to obtain more quantitative data in order to draw more definite conclusions regarding the behaviour of thiophene derivatives (22).

Conclusions.

After studying the photoadditions of carbonyl compounds to the common five-membered heterocycles, furan pyrrole, and thiophene, for several years, from the experience obtained in this laboratory and from the experience of other workers the following conclusions may be drawn:

1.- Furan and its methyl derivatives behave as a system of two double bonds capable of accepting one or two molecules of carbonyl compound to form a single or a double oxetane according to the conditions of the reaction.

2.- In methyl-substituted furans (1) and thiophenes (21) the excited carbonyl compounds react preferably with the double bond with a higher degree of substitution, when carbonyl compounds with triplet energy (T_1) of the same order of magnitude as that of benzophenone are used. With carbonyl compounds of higher triplet energy such as benzaldehyde or propionaldehyde the reaction may occur on either double bond (11).

3.- Thiophene and its monomethyl derivatives are inert to the reaction. Oxetanes are formed when at least two methyl groups are present in the ring. Preliminary studies (22) on the quenching properties of thiophene and its monomethyl derivatives on the photoreduction reaction of benzophenone indicate that thiophene is a good quencher of the reaction and its monomethyl derivatives are even more efficient quenchers than thiophene itself. The reactive excited state both for oxetane formation and photoreduction is the same, namely T_1 (14).

4.- Pyrrole and its methyl derivatives (*N*-methyl and 2,5-dimethylpyrrole) are inert to the oxetane forming reaction, partly, because pyrrole decomposes and turns dark acting as a filter. Furthermore, preliminary studies on the quenching properties of pyrrole on the photoreduction of benzophenone indicate that it is a good quencher at very low concentrations where the darkening is not observable (22).

5.- In the pyrrole series it is necessary to place an electron attracting group such as benzoyl or acetyl on the nitrogen atom to be able to obtain oxetanes. Application of this procedure has been extended to azaindole (23) and imidazoles (24) which are also inert to the reaction if this condition is not fulfilled.

6.- Yields of the oxetane forming reaction improve in the direction pyrrole < thiophene < furan (20, 50, 80% average yield).

7.- Addition of the carbonyl compound to double bonds in the ring always takes place in a *cis* manner and the oxygen of the oxetane ring is always located next to the carbon atom adjacent to the heteroatom in the five-membered ring. This does not apply to the double oxetanes (25).

8.- More work is to be done on the pyrrole and the thiophene series to acquire a better understanding of their behaviour.

9.- With the knowledge acquired throughout the work on furan, pyrrole and thiophene it is possible now to start working with other heterocycles such as selenophene. Selenophene itself is also inert to the reaction as it has been shown in this laboratory (26). However, there is some evidence that substituted selenophenes may be good substrates for excited carbonyl compounds. This information comes from preliminary synthetic experiments.

EXPERIMENTAL

Nuclear magnetic resonance (nmr) data were obtained at approximately 30° using Varian model T-60 and H-60 spectrometers with deuteriochloroform as the solvent and TMS as the internal standard. The mass spectra were determined with a Hitachi-Perkin Elmer RMU-6H mass spectrometer. The elemental analyses were performed by Franz Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Gas chromatographic analyses were carried out by means of a Packard Becker 420 gas chromatograph equipped with a 20% TCEP column. The following reagents: furan, 2-methylfuran, 4-methyl, 4-methoxy and 4-chlorobenzophenone, 2-benzoyl, 2-methyl and 2,5-dimethylthiophene, 1- and 2-naphthaldehyde, 2,2'-dipyridyl ketone and 9-fluorenone were all purchased from Aldrich Chemical Company; the solids were purified by crystallization and the liquids by distillation before use. Benzil was prepared from benzoin according to the method described by Fieser (27). Di-1-naphthyl ketone was prepared by means of a Grignard reaction between 1-naphthylmagnesium bromide and 1-cyanonaphthalene as described by Blicke (28).

Photolysis of 4-Methylbenzophenone in 2-Methylfuran.

A solution of 2 g (0,0102 mole) of 4-methylbenzophenone in 100 ml of 2-methylfuran was placed in a 110 ml reaction vessel. A quartz immersion well containing a pyrex filter sleeve and a Hanovia 450-w lamp was fitted into it. The reaction mixture was irradiated at −10° (Colora Kalte thermostat) for 5 hours; nitrogen gas was passed through the solution before and during the irradiation. After the irradiation was stopped the solvent was distilled and the residue solidified into a mass of crystals of almost pure compound; washing the crystals with petroleum ether was enough to obtain pure oxetane; mp 128-130°, 90% yield. Anal. requires for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.38; H, 6.44.

Other Oxetane Forming Reaction.

These reactions were carried out as illustrated above for 4-methylbenzophenone in 2-methylfuran. The total yields were calculated on the basis of ketone consumed; these and the melting points are given in Table IV.

Non Oxetanic Compounds.

Compounds **11** and **12** were obtained from the corresponding reaction mixtures, by means of column chromatography on neutral alumina, after verifying by thin layer chromatography that the main product of the reaction was different from the expected oxetanes.

The physical constants for compound **11** are as follows: mp 97°, 20% yield; ms: m/e 296 (M^+), 278 (M^+ $-H_2O$), 185 (base peak, di-2-pyridyl ketone + H), 112 (2,5-dimethylthiophene), 111 (2,5-dimethylthiophene-H). The elemental analysis is given in Table V.

The physical constants for compound **12** are as follows: yellowish liquid with thiophene like odor; ms: m/e 222 (M^+), 207 (M^+ $-CH_3$), 163 (M^+ $-SCCH_3$), 111 ($M^+/2$, base peak). It was not possible to obtain a good analysis. Presumably, by the time it arrives at the microanalytical laboratory it has decomposed.

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