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PHOTOCHEMISTRY OF HETEROCYCLIC COMPOUNDS II (1). KETOTRIAZOLES

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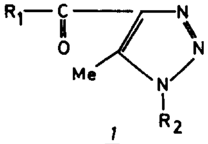
Although the photochemistry of aromatic ketones has been investigated extensively (2a-h) few studies (2i) were performed on the heterocyclic analogues. We wish to report here some results obtained in the study of ketotriazoles with general structure *1* (3).



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	R_1	R_2
a.	C_6H_5	H
b.	CH_3	H
c.	C_6H_5	$p\text{-}C_6H_4\text{-}Cl$
d.	C_6H_5	$p\text{-}C_6H_4Br$
e.	CH_3	$p\text{-}C_6H_4Cl$
f.	CH_3	$p\text{-}C_6H_4Br$

The triazoles were prepared in analogy with a synthesis reported by Fusco and Bianchetti (4). The nature, life-time and the energy level of the lowest lying excited triplet states are reported in table I. The triplet energy levels are higher than those of the phenyl analogues, o-methyl benzophenone *2* and o-methyl acetophenone *3*. The compounds *1c* and *1d* have, in contrast to 4-phenylbenzophenone *4* (5), a $n\pi^*$ low lying triplet state as could be ascertained from the life time, the singlet-triplet splitting (*1c* 2019 cm^{-1}, *1d* 2150 cm^{-1}) and the vibrational structure of the phosphorescence spectra (*1c* 1540 cm^{-1}, *1d* 1570 cm^{-1}). Compounds *1e* and *1f* on the contrary, have a low lying $\pi-\pi^*$ triplet state as indicated by the absence of vibrational structure in the phosphorescence emission spectrum and by the influence of heavy atoms on the triplet life-time. Indeed they have a phosphorescence emission spectrum identical to that of 1-p-bromophenyl-5-methyl-1,2,3-triazole *5*. This also indicates that intramolecular energy transfer from T^1 ($n\pi^*$) of the carbonyl to T^1 ($\pi\pi^*$) of the aromatic system in *1c* and *1d* is energetically not favorable.

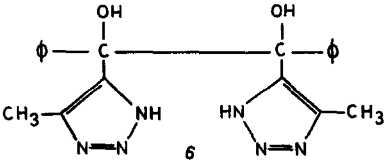
TABLE I

Triplet energy levels and life-times of ketotriazoles

	E_T kcal.$^{(a)}$mol^{-1}	$\tau_{phos.}$ 10^3sec.$^{(b)}$	$\Phi_{ISC}$$^{(c)}$
1a	71.5	5	1
1b	78	1.7	1
1c	71.3	5	0.99
1d	71.1	5	0.96
1e	78.4$^{(d)}$	58	-
1f	78.4$^{(d)}$	7	-
2	70	4.2	-
3	73	72	-
5	78.4$^{(d)}$	8	-

(a) triplet energy level measured at 77°K in E.P.A.;
(b) measured by flash photolysis at 77°K in E.P.A.;
(c) measured by triplet counting with piperylene;
(d) onset of phosphorescence emission, maximum at 69 kcal.mol^{-1}

Compound *1a* is on irradiation in isopropanol reduced quantitatively to pinacol *6*. The structure of the pinacol could be ascertained from the absence of the carbonyl stretching and appearance of OH stretching at 3380 cm^{-1} in IR, the change of the pattern of the aryl protons in NMR and the molecular ion (M^+ 376) in MS.



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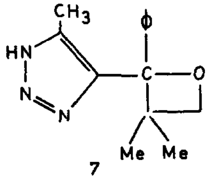
Compound *1a* adds also quantitatively to isobutylene to form oxetane *7*.



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The structure of *7* could be determined on the basis of MS : M^+ 243 ; of IR : C-O 980 cm^{-1} and absence of the carbonyl function and of NMR absorption of the methylene ring protons at 4.32 δ ($O-CH_2-$).
The values for k_r, the rate constant of hydrogen abstraction and k_d the rate constant for triplet desactivation were determined for *1a* and *2* from the quantum yield of photoreduction in presence of naphtalene as quencher and are reported in table II.

TABLE II

Rate constants for photoreduction in isopropanol$^{(a)}$

	k_q $l.mole^{-1}sec^{-1}$	k_r $l.mole^{-1}sec^{-1}$	k_d sec^{-1}
Benzophenone$^{(b)}$	$3.2\ 10^9$	$1.5\ 10^6$	$1.5\ 10^5$
1a	$3.2\ 10^9$	$2.5\ 10^6$	$1.3\ 10^6$
2	$3.2\ 10^9$	$1.7\ 10^4$	$5\ \ 10^5$

(a) $[\ Q\ ] = 10^{-3} - 10^{-4}$ $mol.l^{-1}$

(b) see reference 2a

The reported data indicate that the low quantum yield of photoreduction of o-methylbenzophenone is not primarily due to enol formation but most probably to mixing of $n\pi^*$ and $\pi\pi^*$ triplet levels at the temperature of the reaction.
Attempts to observe enol formation of *1a* by trapping or by exchange with deuterium showed no evidence for the intramolecular hydrogen abstraction. The high k_d

value of *1a* can however be explained by interaction of the lone pair electrons of the nitrogen with the excited carbonyl functions. Further work on analogous systems will be reported in the near future.

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