Ultraviolet Absorption of *trans*-3-Halo-2-decalones

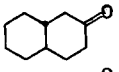
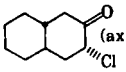
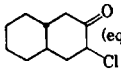
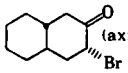
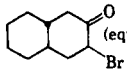
By O. KRISTIANSEN, E. E. SMISSMAN, and E. M. KOSOWER*

THE AVAILABILITY of some *trans*-3-halo-2-decalones from other research (1) allowed an examination of the solvent effect on the $n \rightarrow \pi^*$-transition. The results of the investigation of the ultraviolet spectra of these ketones in a series of solvents chosen for their range of Z-values (2) are reported in Table I.

The pattern of results for the 3-halo-2-decalones resembles that previously summarized for the conformationally fixed cyclohexanones (3). The change in $n \rightarrow \pi^*$-transition energy on substitution is fairly similar in both series as shown by the Δ-values listed in Table II.

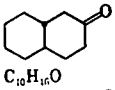
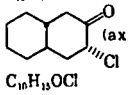
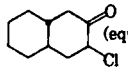
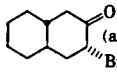
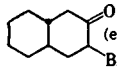
As noted before (3), the solvent sensitivities of the $n \rightarrow \pi^*$ transitions of the halo ketones is considerably lower than that for the unsubstituted ketones. It is imperative, then, that derived quantities (like Δ) for which some attempt at theoretical interpretation is made be recorded in the same nonpolar solvent.

TABLE II.—Δ-VALUES

	Δ (Kcal./mole)[a]	Cyclohexanones[a, b]
		
 (axial)	−5.42	−4.7
 (equat.)	+0.58	+1.89
 (axial)	−7.02	−7.4
 (equat.)	+0.59	+0.2

[a] Represents the difference in the $n \rightarrow \pi^*$ transition energy of the derivative and the parent ketone in a nonpolar solvent. [b] *Reference 3.*

TABLE I.—ULTRAVIOLET SPECTRA OF KETONES[a]

	Solvent			
	Isooctane (60.1)[b] $\lambda_{max.}$, Å.(ε$_m$)	Acetonitrile (71.3)[b] $\lambda_{max.}$, Å.(ε$_m$)	Methanol (83.6)[b] $\lambda_{max.}$, Å.(ε$_m$)	Water (94.6)[b] $\lambda_{max.}$, Å.(ε$_m$)
 $C_{10}H_{16}O$	2885 (18) 99.10	2845 (19) 100.49	2825 (22) 101.20	2783 102.73
 (axial) $C_{10}H_{15}OCl$	3052 (41) 93.68	3038 (44) 94.11	3026 (37) 94.48	...
 (equat.)	2868 (20) 99.68	2878 (23) 99.34	2846 (24) 100.46	...
 (axial)	3105 (104) 92.08	3103 (102) 92.14	3038 (102) 92.73	...
 (equat.)	2868 (28) 99.69	2855 (30) 100.14	2838 (31) 100.74	... ...

[a] Transition energies are given in Kcal./mole immediately below the figure for $\lambda_{max.}$. [b] Z-value (*Reference 2*).

Received December 27, 1963, from the Department of Pharmaceutical Chemistry, School of Pharmacy, The University of Kansas, Lawrence.
Accepted for publication March 9, 1964.
* Present address: Department of Chemistry, State University of New York, Long Island Center, Oyster Bay.
This work was supported by Grant EF209, U. S. Public Health Service, Bethesda, Md.

REFERENCES

(1) Kristiansen, O., and Smissman, E. E., unpublished results.
(2) Kosower, E. M., *J. Am. Chem. Soc.*, 80, 3253(1958).
(3) Kosower, E. M., Wu, G. S., and Sorenson, T. S., *ibid.*, 83, 3147(1961).