[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Absorption Spectra of Some 2,4-Dinitrophenylhydrazones

BY JOHN D. ROBERTS[1] AND CHARLOTTE GREEN

It has been pointed out by Redemann[2] that the crystalline 2,4-dinitrophenylhydrazones of α,β-unsaturated carbonyl compounds are usually bright red in contrast to the yellow colors of the corresponding saturated derivatives. In view of the widespread interest in the use of 2,4-dinitrophenylhydrazones as derivatives for the identification and characterization of carbonyl compounds, coupled with the fact that a number of exceptions are known to the above-mentioned color rule, we have undertaken a study of the absorption spectra of a number of dinitrophenylhydrazones in neutral and alkaline solutions to see if more reliable criteria for the structure and degree of unsaturation of the original compounds could be obtained.

Experimental

The 2,4-dinitrophenylhydrazones were prepared by the customary methods.[3] The melting points and colors of the solid derivatives as well as the solvents used for recrystallization are given in Table I.

The absorption spectra were taken of solutions of appropriate concentrations (10–20 mg./liter) using the Beckman Quartz Spectrophotometer.[4] Commercial 95% alcohol was the customary solvent. Spectra were also taken of alkaline alcoholic solutions which were prepared by diluting stock solutions of the derivatives with alcoholic potassium hydroxide.

Discussion

The general appearance of the spectral absorption curves for crotonaldehyde 2,4-dinitrophenylhydrazone in three solvents is shown in Fig. 1. The curves for hexane and carbon tetrachloride solutions are quite similar, although the value of the maximum extinction coefficient, $\epsilon_{max.}$, is somewhat lower for the latter solution. In ethyl alcohol the wave length of maximum absorption, $\lambda_{max.}$, is shifted about 20 mμ toward the visible.

Absorption curves for some dinitrophenylhydrazones of different types of carbonyl compounds are shown in Fig. 2. In common with the spectra obtained with a series of carbonyl compounds, increasing substitution of alkyl groups for hydrogen atoms located alpha to an unsaturated linkage[5,6] and increasing degree of conjugated un-

TABLE I

PHYSICAL PROPERTIES AND ABSORPTION MAXIMA OF 2,4-DINITROPHENYLHYDRAZINE AND ITS DERIVATIVES

No.	Compound	M. p., °C.	Recryst. solvent	Color[a]	$\lambda_{max.}$[b] (mμ)	$\epsilon_{max.}$[b]
1	2,4-Dinitrophenylhydrazine	200.5–201.5	....	OR	352[c]	14,900[c]
2	Formaldehyde DNPH[d]	164.8–165.3	C_2H_5OH	Y	349	18,200
3	Acetaldehyde DNPH	164–164.5	C_2H_5OH	Y	356	21,000
4	Methylvinylacetaldehyde DNPH	122.8–123.5	C_2H_5OH	O	357	21,600
5	2-Methylbutyraldehyde DNPH	128–128.5	C_2H_5OH	Y	358	22,000
6	Propionaldehyde DNPH	154.5–155	C_2H_5OH	O	359	21,800
7	Acetone DNPH	125–126.5	C_2H_5OH	Y	360	21,100
8	Cyclopentanone DNPH	144–145	C_2H_5OH	Y	363	21,500
9	Diisopropyl ketone DNPH	91–92	C_2H_5OH	Y	363	22,000
10	Cyclopropyl methyl ketone DNPH	149–150	C_2H_5OH	OR	367	23,500
11	Crotonaldehyde DNPH	187–188	CH_3CO_2H	R	377[e]	26,600[e]
12	Tiglaldehyde DNPH	215.5–217.5	$CH_3CO_2C_2H_5$	R	377	27,500
13	Benzaldehyde DNPH	238–239	CH_3CO_2H	O	378	29,200
14	Mesityl oxide DNPH	198.5–199.5	CH_3CO_2H	R	379	23,000
15	Benzophenone DNPH	240–241	CH_3CO_2H	O	383	28,300
16	*p*-Methylacetophenone DNPH	257–258	CH_3CO_2H	R	383	27,600
17	Salicylaldehyde DNPH	250–252	CH_3CO_2H	R	387	29,500
18	Cinnamaldehyde DNPH	252–253	CH_3CO_2H	R	394	38,000
19	*p*-Hydroxybenzaldehyde DNPH	280d.	$C_6H_5NO_2$	RV	395	28,700
20	Chalcone DNPH	247–248	CH_3CO_2H	OR	395	36,400

[a] The colors of the crystalline derivatives appear to be consistent with the following generalization: if the solid derivative is bright red the parent compound is an α,β-unsaturated or an aromatic carbonyl compound, if it is yellow the parent substance is probably not of these types and if it is orange or an intermediate shade no definite conclusions can be drawn. There is no apparent relation between the colors of the solids and the number of conjugated double bonds in the original carbonyl compound. [b] Solvent, 95% alcohol. [c] McBeth and Price, *J. Chem. Soc.*, 1563 (1935), report $\lambda_{max.}$ 352 mμ and $\epsilon_{max.}$ 14,000. [d] DNPH is 2,4-dinitrophenylhydrazone. [e] Marvel and Inskeep, THIS JOURNAL, **65**, 1710 (1943), report $\lambda_{max.}$ 375 mμ and $\epsilon_{max.}$ 30,000. *Anal.* Calcd. for $C_{11}H_{12}O_4N_4$: C, 49.99; H, 4.57. Found: C, 49.69; H, 4.36.

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(1) Present address: Department of Chemistry of Harvard University, Cambridge 38, Mass.

(2) Buchman, Schlatter and Reims, THIS JOURNAL, **64**, 2701 (ref. 18) (1942).

(3) (a) Allen, *ibid.*, **52**, 2955 (1930); (b) Allen and Richmond, *J. Org. Chem.*, **2**, 222 (1937).

(4) Cary and Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

(5) Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41, 1770 (1941).

(6) Woodward, *ibid.*, **63**, 1123 (1941).

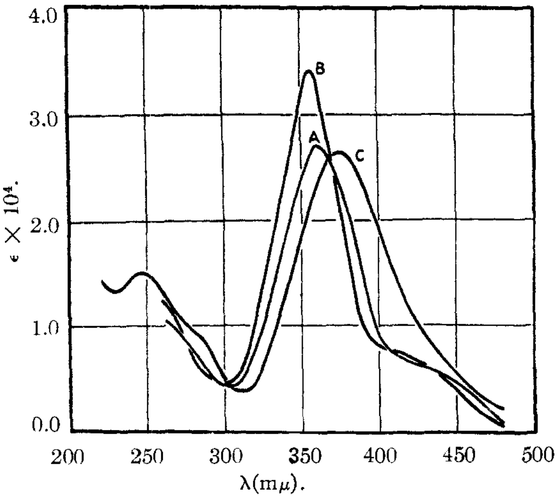


Fig. 1.—Absorption spectra of crotonaldehyde DNPH in different solvents: A, carbon tetrachloride; B, hexane; C, ethanol (95%).

saturation cause shifts of the absorption maxima toward the longer wave lengths. In general, the effects of the substitution of alkyl groups on the spectra of the hydrazones are much smaller than those observed in the corresponding carbonyl compounds[6] (compare 3, 5, 6, 7 and 9 or 11 and 12 of Table I) and should have but little diagnostic value for elucidating specific structures. On the other hand, the values of $\lambda_{max.}$ and $\epsilon_{max.}$ for different types of unsaturated compounds appear to fall in definite ranges and should be of considerable practical utility in determining the degree of conjugated unsaturation of unknown carbonyl compounds, particularly in those cases where the carbonyl compound itself is difficult to separate or purify.[7] In general, the absorption maxima of dinitrophenylhydrazones with no double bonds conjugated with the imino linkage fall in the range 349–363 mμ with values of $\epsilon_{max.}$ ranging from 18,000–22,000 (compounds 2–9 of Table I). Those having one double bond or unsubstituted aromatic ring (11–14) conjugated with the imino linkage show maxima of 377–379 mμ with corresponding $\epsilon_{max.}$ values of 26,600–29,200. As might be expected from the studies of Carr and Burt[8] and Klotz[9] the values of $\lambda_{max.}$ and $\epsilon_{max.}$ for the absorption curve of the dinitrophenylhydrazone of cyclopropyl methyl ketone are between those for saturated and α,β-unsaturated carbonyl compounds. Derivatives with aromatic rings conjugated with double bonds (18 and 20) show maxima at 394–395 mμ with $\epsilon_{max.}$ values in the neighborhood of 38,000. No extensive study of the effects of substituent groups on the spectra of aromatic carbonyl compounds was undertaken in the present work but it may be pointed out that substitution of hydroxyl for hydrogen in the ortho and para positions of benzaldehyde causes shifts of $\lambda_{max.}$ of 9 and 17 mμ, respectively, without essentially changing the values of $\epsilon_{max.}$.

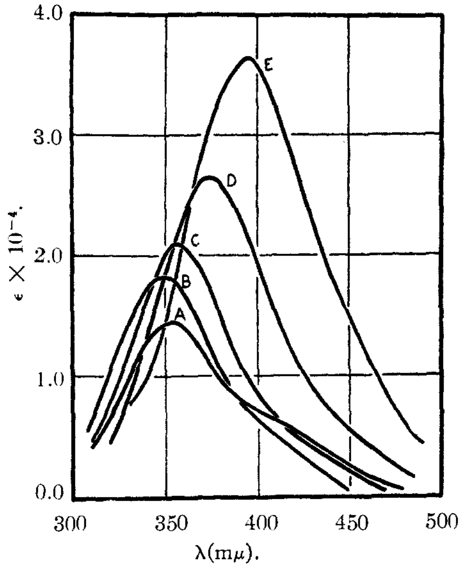
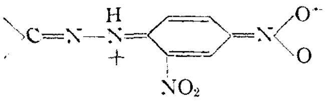


Fig. 2.—Absorption spectra of 2,4-dinitrophenylhydrazine and its derivatives in 95% ethanol: A, 2,4-dinitrophenylhydrazine; B, formaldehyde DNPH; C, acetaldehyde DNPH; D, crotonaldehyde DNPH; E, chalcone DNPH.

It is interesting to note that the shifts in absorption maxima resulting from increased conjugation in the hydrazones are considerably smaller than those observed for similar changes in the corresponding carbonyl compounds.[10] As the absorption curve for 2,4-dinitrophenylhydrazine is similar to those of the hydrazones the effects of substituents located on the carbonyl moiety of the derivative on the principal absorption maximum must be to modify the absorption bands principally due to the dinitrophenyl half of the molecule. The influence of a given structural change is probably not so strongly transmitted across the $=N-\overset{H}{N}-$ linkage as it would be across a conjugated system of multiple bonds. However, the hydrazine half of the molecule is not truly isolated as variations in the carbonyl part should certainly influence the relative importance of contributions of forms such as



to the resonance hybrid by influencing the relative contributions of forms such as

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[7] The large increase in $\epsilon_{max.}$ associated with the conversion of a carbonyl compound to its dinitrophenylhydrazone suggests possible applications to the quantitative analysis of aldehydes and ketones.

[8] Carr and Burt, THIS JOURNAL, **40**, 1590 (1918).

[9] Klotz, *ibid.*, **66**, 88 (1944).

[10] The spectra of oximes, semicarbazones and thiosemicarbazones appear to be somewhat more sensitive to changes of structure in the carbonyl moiety of the derivatives. *Cf.* Evans and Gillam, *J. Chem. Soc.*, 565 (1943).

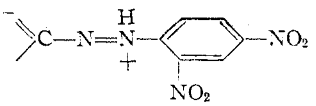

TABLE II

SPECTRA OF 2,4-DINITROPHENYLHYDRAZINE AND ITS DERIVATIVES IN ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION

Compound	$\lambda_{max.}$[a] ($m\mu$)	$\epsilon_{max.}$[a]	$\Delta\lambda_{max.}$[c]
2,4-Dinitrophenylhydrazine	395?[b]	2,600	43?
Formaldehyde DNPH	410?[b]	5,000	61?
Acetaldehyde DNPH	425	16,200	69
Crotonaldehyde DNPH	451	29,900	74
Benzaldehyde DNPH	467	33,000	89
p-Hydroxybenzaldehyde DNPH	482	32,300	87
Chalcone DNPH	516	24,600	121

[a] Solution in 0.12 *N* alcoholic potassium hydroxide. [b] Broad maximum with uncertain peak. [c] $\Delta\lambda_{max.} = \lambda_{max.}$ (alkaline solution) − $\lambda_{max.}$ (neutral solution).

The colors of solutions of dinitrophenylhydrazones are usually greatly changed by the addition of alkali and we have studied the absorption spectra of several of the derivatives in alcoholic potassium hydroxide solution. The results are given in Table II. In every case $\lambda_{max.}$ in neutral solution was shifted toward the visible by adding alkali. A somewhat greater shift was observed for the more unsaturated compounds. No consistent effect on $\epsilon_{max.}$ was found. In some cases $\epsilon_{max.}$ was considerably increased, in others it was lowered to one-third or less of its original value.

Summary

The absorption spectra of some 2,4-dinitrophenylhydrazones have been studied and related to the structure of the corresponding carbonyl compounds.

CAMBRIDGE, MASS. RECEIVED OCTOBER 23, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

The Ultraviolet Absorption Spectra of Dioxadiene and Dioxene

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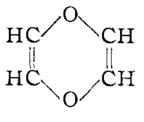
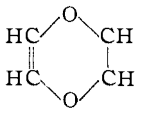
The present study of the ultraviolet absorption spectra of dioxadiene (also called *p*-dioxin) and dioxene (or 2,3-dihydro-*p*-dioxin) is in continuation of an extensive investigation of the absorption spectra of unsaturated hydrocarbons in this Laboratory.[1] This study has included both acyclic and cyclic alkenes and dienes and has been extended to certain heterocyclic compounds such as furan[2] which may be considered as related to hydrocarbons by the substitution of oxygen for a methylene group. Dioxadiene and dioxene may thus be compared with 1,4-cyclohexadiene and cyclohexene, respectively.





Both compounds were first prepared by Summerbell and co-workers[3] whose reports of their preparation and properties are the only record of them so far found in the literature with the exception of a study[4] of their configuration by electron diffraction. Dioxadiene in particular is of especial interest for spectral studies because of its high degree of symmetry and the comparatively small number of atoms present in the molecule. Its spectrum is very distinct, showing five electronic transitions with well marked vibrational patterns.

Experimental

Preparation and Purification of Compounds[5]

Dioxene was prepared from 2,3-dichlorodioxane by the method reported by Summerbell[3] and purified by fractional distillation through a 40-cm. Fenske column in an atmosphere of nitrogen. The fraction used in the measurements boiled at 94.1° at 760 mm., and its physical constants (d^{20}_4 1.0836, n^{20}D 1.4372) agreed with those of Summerbell.

Dioxadiene was similarly prepared from 2,3,5,6-tetrachlorodioxane. The preparation of the latter is of interest because of the number of stereoisomers as well as position isomers which can be formed when dioxane is chlorinated. A number of these have been isolated. Butler and Cretcher[6] obtained two symmetrical tetrachlorodioxanes melting, respectively, at 59–60° and 143–144°. Christ and Summerbell[7] reported symmetrical isomers melting at 143 and 70°. A 101°[8] isomer has also been reported. In the present work, mixtures were separated by fractional distillation to yield products melting at 143–144, 70 and 58–59° as well as liquid unsymmetrical isomers. The structures of the different products were ascertained by an identification of the products of hydrolysis. The solid products mentioned here are three of the five theoretically possible stereoisomers of symmetrical tetrachlorodioxane.

The dioxadiene used in the present work was prepared from the isomer melting at 58–59°, while Summerbell and Umhoefer[3] obtained their product from the isomer melting at 143°. The physical constants of the material used,

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[1] E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); **6**, 55 (1938); E. P. Carr, L. Pickett and H. Stücklen, *Rev. Mod. Phys.*, **14**, 260 (1942).

[2] L. Pickett, *J. Chem. Phys.*, **8**, 293 (1940).

[3] R. K. Summerbell and L. N. Bauer, THIS JOURNAL, **57**, 2364 1935); R. K. Summerbell and R. R. Umhoefer, *ibid.*, **61**, 3020 (1939).

[4] J. Y. Beach, *J. Chem. Phys.*, **9**, 54 (1941).

[5] The synthesis and purification of these compounds were carried out under the direction of Dr. Mary L. Sherrill. The authors are also indebted to Miss Jean Lamont for the preparation and preliminary studies of dioxene and 1,4-cyclohexadiene.

[6] C. L. Butler and L. H. Cretcher, THIS JOURNAL, **54**, 2987 (1932).

[7] R. Christ and R. K. Summerbell, *ibid.*, **55**, 4547 (1933).

[8] W. Baker, *J. Chem. Soc.*, 2666 (1932).