Tropones. IV. Ultraviolet Absorption Spectra of Reaction Products of Tropones and Carbonyl Reagents***

By Toshio MUKAI

(Received June 8, 1959)

The reaction products of tropone and carbonyl reagents, such as oxime, semicarbazone, thiosemicarbazone, phenylhydrazone, and nitrophenylhydrazone form peculiar conjugation systems and they are of interest in the study of ultraviolet spectrum. These compounds generally have deep color, ranging from orange to dusky purple. The present paper describes observations on the ultraviolet spectra of products obtained on the reaction of tropone and tropones possessing the methyl, phenyl, naphthyl, *o*-tolyl, or benzyl group in 2-position, and carbonyl reagents, measured in methanol, acidic and alkaline solutions.

The ultraviolet spectrum of tropone oxime1), of tropone semicarbazone1) and of tropone thiosemicarbazone are shown in Figs. 1—3, respectively. These three compounds possess a C=N– group in place of the carbonyl group in tropone and show two typical absorption maxima as tropone itself does1). The maximum absorption in methanol solution shifts to longer wavelengths in the order of the oxime, semicarbazone and thiosemicarbazone, and this tendency is the same as that in the case of unsaturated ketone derivaives in general2). All three compounds have fairly deep color which must be due to the broad absorption appearing at the wavelength region above 400 mμ.

The ultraviolet spectra of the oxime and semicarbazone in hydrochloric acid solution show a shift to a longer wavelength region and that of the thiosemicarbazone to slightly shorter wavelengths. The absorption maxima lie near 240 and 330 mμ in all three compounds and the value of their intensity is also similar.

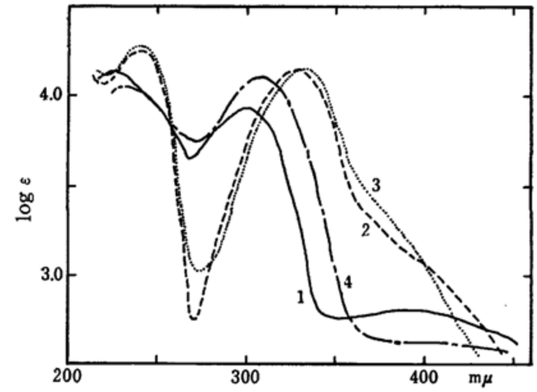


Fig. 1. Ultraviolet absorption spectra of tropone oxime: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

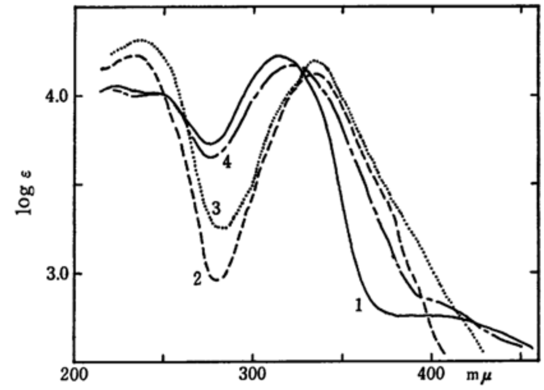


Fig. 2. Ultraviolet absorption spectra of semicarbazone of tropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1N NaOH solution.

This fact indicates that they all have a structure of conjugate acid like I and that their absorptions are not so greatly affected by group R. The fact that there is no shift of the absorption curve according to the concentration of hydrochloric acid (in 0.1 or 6 N), suggests that the formation of the conjugate acid (I) is almost complete even in dilute acid solution such as 0.1 N solution.

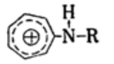
---

* Part I: Ref. 1; Part II: T. Mukai, This Bulletin, **31**, 846 (1958); Part III: Ref. 3.

** Presented before the 39th Tohoku Local Meeting of the Chemical Socity of Japan, Sendai, May, 1956.

1) T. Nozoe, T. Mukai and T. Takase, *Sci. Repts. Tohoku Univ., First Ser.*, **39**, 164 (1956).

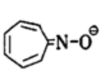
2) A. E. Gillam and E. S. Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry ", Edward Arnold Publishers, Ltd., London (1955), p. 100.



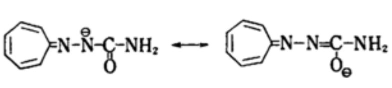
(I)

R=OH, NHCONH₂, NHCSNH₂

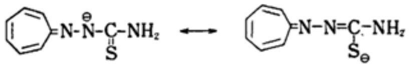
In alkaline solution, the absorption curves of the oxime, semicarbazone and thiosemicarbazone, all show a shift to a longer wavelength region. It has already been pointed out that the oxime has an amphoteric property, is stable, and dissolves both in acids and in alkalis¹⁾, and this shift is assumed to be due to the formation of an anion (II). Similarly, formation of anions (III) and (IV) can be expected for the semicarbazone and thiosemicarbazone.



(II)



(III)



(IV)

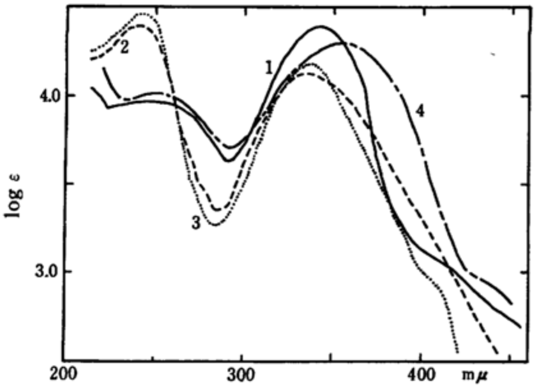


Fig. 3. Ultraviolet absorption spectra of thiosemicarbazone of tropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1N NaOH solution.

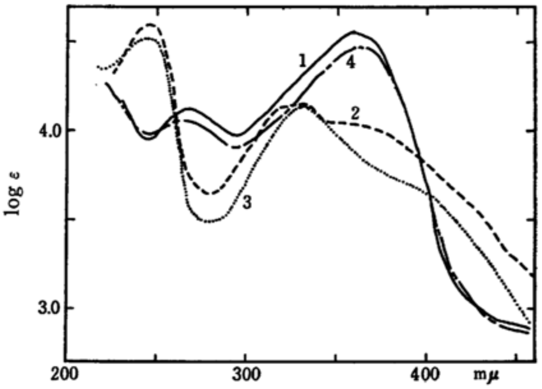


Fig. 4. Ultraviolet absorption spectra of *p*-bromophenylhydrazone of tropone: (1) in methanol, (2) in 0.1 N HCl (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

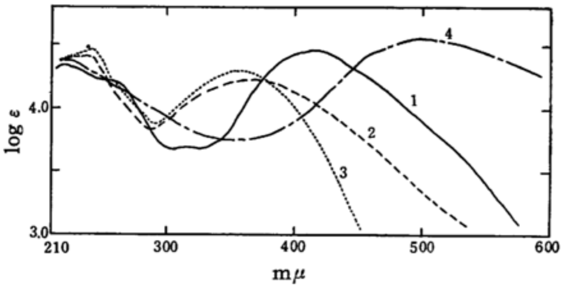


Fig. 5. Ultraviolet absorption spectra of 2,4-dinitrophenylhydrazone of tropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

Ultraviolet absorption spectra of the phenylhydrazone¹⁾ and *p*-bromophenylhydrazone¹⁾ of tropone are shown in Table I and Fig. 4 and those of *p*-nitrophenylhydrazone¹⁾ and 2,4-dinitrophenylhydrazone¹⁾ of tropone in Table I and Fig. 5. These phenylhydrazones exhibit absorption maximum at a longer wavelength region than the oxime and semicarbazone do. Further it is seen that the introduction of a nitro group in the

TABLE I. ABSORPTION MAXIMA OF TROPONE DERIVATIVES IN mμ (log ε)

	MeOH	0.1 N HCl	6 N HCl	0.1 N NaOH
Phenylhydrazone	256(4.11) 355(4.43)	240(4.41) 328(4.05)		252(3.97) 355(4.33)
p-Nitrophenylhydrazone	255(inf) 315(3.78) 383(3.83) 429(4.55)	237(4.42) 356(4.40)	237(4.42) 350(4.27)	255(sh) 303(3.83) 510(4.27)
2,4-Dinitrophenylhydrazone	219(4.34) 260(4.20) 315(3.70) 413(4.45)	237(4.40) 363(4.23)	238(4.45) 353(4.29)	220(sh) 500(4.53)

TABLE II. ABSORPTION MAXIMA OF OXIMES IN mμ (lon ε)

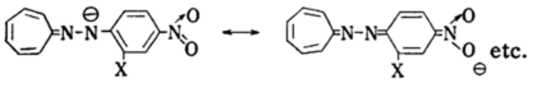
	MeOH	0.1 N HCl	6 N HCl	0.1 N NaOH
2-Methyltropone	228(4.24)	243(4.31)	243(4.36)	236(4.16)
	300(3.85)	338(4.09)	338(4.11)	303(3.90)
	360(2.91)*			
	390(2.91)*			
2-Phenyltropone	222(4.20)	237(4.23)	238(4.33)	235(4.14)
	260(4.04)	345(3.95)	341(4.06)	265(4.05)
	307(3.75)			308(3.70)
2-Benzyltropone	228(4.21)	240(4.27)	243(4.35)	243(4.15)
	300(3.78)	339(3.98)	340(4.11)	303(3.85)
	358(2.93)*			
	380(2.93)*			
2-α-Naphthyltropone	222(4.89)	222(4.92)	224(4.86)	223(4.84)
	293(4.04)	240(4.28)	245(4.30)	297(3.97)
	380(3.17)*	280(3.83)	334(3.99)	
		336(4.01)		
2-*o*-Tolyltropone	295(3.82)	240(4.27)	240(4.37)	238(4.21)
	ca. 355(3.10)*	340(4.00)	339(4.11)	308(3.90)

* Broad band. These bands can not be compared with each other.

ortho- or para-position of the phenyl ring results in a further shift of the maximum to a longer wavelengths (above 400 mμ).

In hydrochloric acid solution, they all show a shift originating in the formation of a conjugate acid [I : R= $-NH-C_6H_5$, $-NH-C_6H_4Br$(*p*), $-NH-C_6H_4NO_2$(*p*), $-NH-C_6H_3(NO_2)_2$(2, 4)]. In *p*-nitro- and 2, 4-dinitrophenylhydrazones, there is a shift of 6～10 mμ when the concentration changes from 0.1 to 6 N hydrocholric acid. This is probably due to the weakened basicity of these compounds by the introduction of a nitro group which has an effect on the formation of the conjugate acid (I).

In alkaline solution, the absorption maxima of *p*-nitro and 2, 4-dinitrophenylhydrazone shift to a longer wavelength region (above 500 mμ) and this is due to the formation of an anion (V) with a long chain of conjugation. The formation of an anion (V) is supported by the fact that phenylhydrazone and *p*-bromophenylhydrazone hardly show any shift in alkaline solution (see Fig. 4).



(V) X=H . NO_2

The ultraviolet absorption spectra of *p*-nitrophenylhydrazone in methanol and alkaline solution exhibit maxima at somewhat longer wavelength than that of 2, 4-dinitrophenylhydrazone and this is due to the steric hindrance of the nitro group in 2-position of the phenyl ring. However, the maximum of 2, 4-dinitrophenylhydrazone appears in a longer wavelength than that of *p*-nitrophenylhydrazone in acid solution. This is probably due to the fact that resonance represented by V occurs only to a small extent in acid solution and consequently the interference of the nitro group in 2-position of the phenyl group does not give an effect on the spectrum.

Of these products from reaction with carbonyl reagents, oxime and 2, 4-dinitrophenylhydrazone are easily formed in tropones possessing alkyl or aryl radical in its 2-position. Effect of a substituent on the ultraviolet spectrum was examined with oximes. Ultraviolet spectra of oximes are shown in Table II.

The absorption maxima of 2-methyltropone oxime[3] in longer wavelength region shift to a slightly shorter wavelengths than those of tropone oxime when measured in methanol or 0.1 N sodium hydroxide solution but conversely shift to a longer wavelength in hydrochloric acid solution. Of these oximes, the interesting thing is the absorption of 2-phenyltropone oxime[4]. As will be seen from Fig. 6, the curve appears different since new absorption maxima appear at

---

[3] T. Mukai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1547 (1958).

[4] T. Nozoe, T. Mukai, J. Minegishi and T. Fujisawa, *Sci. Repts. Tohoku Univ., First Ser.*, **37**, 388 (1954).

TABLE III. ABSORPTION MAXIMA OF 2,4-DINITROPHENYLHYDRAZONE IN mμ (log ε)

	MeOH	0.1 N HCl	6 N HCl	0.1 N NaOH
2-Methyltropone	222(4.36)	239(4.44)	243(4.56)	491(4.40)
	317(3.65)	391(4.24)	354(4.36)	
	410(4.43)			
2-Phenyltropone	232(4.43)	228(4.20)	238(4.25)	ca. 250(4.20)
	405(4.44)	257(4.08)	363(4.05)	498(4.30)
		403(4.12)		
2-Benzyltropone	260(4.17)	410(4.35)	243(4.43)	255(4.30)
	411(4.36)		358(4.23)	490(4.45)
2-α-Naphthyltropone	222(4.97)	222(4.96)	222(4.93)	223(4.94)
	260(4.28)	406(4.32)	241(4.50)	490(4.37)
	410(4.38)		355(4.30)	
2-*o*-Tolyltropone	260(4.26)	240(4.41)	242(4.51)	480(4.17)
	408(4.42)	401(4.33)	358(4.32)	

260 and 265 mμ in methanol and alkali solution. It is considered that the absorption in this region is due to the coplanarity of the seven-membered ring and phenyl ring, as in the case of 2-phenyltropone itself[3,7].

On the other hand, the absorption of 2-benzyltropone oxime[5] is very similar to that of 2-methyltropone by the introduction of a methylene group, while the absorption of 2-α-naphthyltropone oxime does not exhibit the maximum at around 260 mμ seen in the case of 2-phenyltropone oxime, irrespective of the presence of the naphthyl group. Moreover, the second absorption maximum of 2-naphthyltropone oxime have shifted to a shorter wavelength region than the corresponding absorption maximum of 2-phenyltropone oxime in methanol solution (Table II) and a steric interference between the tropone ring and the naphthyl group at peri-position may be considered at its cause. The absorption maximum at 222~224 mμ of strong intensity seen in 2-α-naphthyltropone oxime is thought to be the absorption of naphthalene itself[8]. The ultraviolet spectrum of 2-*o*-tolyltropone oxime[3] also suggests the presence of a steric hindrance by the methyl group in the ortho-position of the phenyl ring. Owing to this effect, this compound has a maximum at 295 mμ which is considerably shifted toward shorter wavelength compared with a maximum of phenyltropone oxime at 307 mμ.

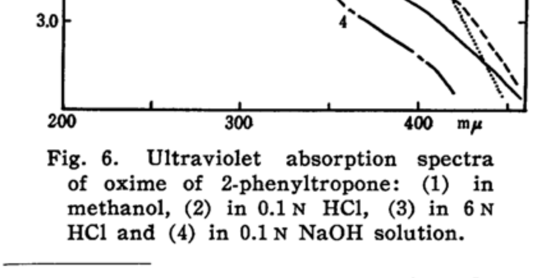


Fig. 6. Ultraviolet absorption spectra of oxime of 2-phenyltropone: (1) in methanol, (2) in 0.1 N HCl, (3) in 6 N HCl and (4) in 0.1 N NaOH solution.

Ultaviolet absorption spectra of 2,4-dinitrophenylhydrazones of various tropones are shown in Table III. In these cases also, the direction of the shift in hydrochloric acid and alkali solutions are the same as in the case of 2,4-dinitrophenylhydrazone of tropone, but the relationship between the shift of absorption and kind of substituents is complicated and conclusive explanation is difficult. The marked tendency of these is the small of shift in the absorption of 2-phenyl-, 2-benzyl- and 2-α-naphthyl-tropone derivatives measured in 0.1 N hydrochloric acid solution. The reason for this is the smallness in basicity and it may be considered that the stronger the basicity, the larger will be the shift. In 6 N hydrochloric acid solution, all the compounds

---

5) T. Nozoe, T. Mukai and I. Murata, *Proc. Japan Acad.*, **29**, 169 (1953).

6) K. Kikuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1439 (1956).

7) R. D. Haworth and P. B. Tinker, *J. Chem. Soc.*, **1955**, 911.

8) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers. Ltd., Londno (1955), p. 122.

have absorption maximum at about 360 mμ and formation of conjugate acids of similar structure may, therefore, be assumed. The absorption maximum of 2-α-naphthyltropone derivative at 222～223 mμ of strong intensity is that of naphthalene itself⁽8⁾, as was stated earlier.

The author takes this opportunity to express his sincere gratitude Professor Tetsuo Nozoe for his kind guidance throughout the course of this work, and to Professor Shuichi Seto and Assistant Professor Yoshio Kitahara for much helpful advice.

Department of Chemistry
Faculty of Science
Tohoku University
Katahiracho, Sendai