ARYL ACETOACETATES—INFRARED AND ULTRAVIOLET SPECTRA

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ABSTRACT.—A series of aryl acetoacetates has been prepared and their infrared and ultraviolet spectra have been determined in order to study the effect of the aryl group upon the keto-enol spectroscopic peak positions.

It is well known that the infrared spectra of beta-ketoesters in the carbonyl region reveal frequencies due to both the keto and enol forms. Although work has been reported correlating spectra of various alkyl acetoacetates and alpha-substituted acetoacetates (Bellamy, 1958), study of the infrared spectra of aryl acetoacetates has not been reported.

The enol form of beta-ketoesters absorbs ultraviolet radiation, and alkyl acetoacetates are reported to absorb in a narrow region around 240 nm (Korte and Wusten, 1961). It is surprising that almost no work has been reported concerning ultraviolet absorption of aryl acetoacetates.

METHODS AND MATERIALS

The aryl acetoacetates were prepared by the method of Zavialov (1965); the physical constants of reported esters agree with values reported by Lacey (1954).

Table 1 gives the data on four unreported esters. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, Tennessee

Infrared spectra were run in spectral grade chloroform in 0.1mm cells on a Beckman IR8 grating spectrophotometer with an auxiliary recorder used for scale expansion. In order to provide absorption maxima for calibration, the 1944 cm^{-1} peak of polystyrene was recorded and, without stopping the scan, the polystyrene was replaced with the cells and the four peaks of interest were recorded. The cells were removed, again without stopping the scan, and replaced with polystyrene and the 1181 and 1154 cm^{-1} peaks were recorded. The above three polystyrene peaks were used for calibration; the error of measurement is estimated to be ± 3cm^{-1}.

UV spectra were run in absolute ethanol on a Beckman DB spectrophotometer with an estimated error of ± 2nm.

RESULTS AND DISCUSSION

Infrared spectra frequencies measured in chloroform are shown in Table 2 and are arranged in decreasing order of the high frequency bands of the ester carbonyl bond. Assignment of the frequencies to the ester carbonyl (1764-1734 cm^{-1}), keto carbonyl (1720-1713 cm^{-1}), enol ester carbonyl (1673-1630 cm^{-1}) and

TABLE 1. Unreported Aryl Acetoacetates

Aryl Group	mp (°C)	Elemental Analysis			
		Calcd		Found	
		% C	% H	% C	% H
p-nitrophenyl	67-69	53.82	4.06	53.66	4.19
2,4,6-trimethylphenyl	60.5-62	70.89	7.32	70.76	7.34
alpha-phenyl-*p*-cresyl	54-56	75.82	6.36	75.82	6.12
2,6-dimethoxyphenyl	64.5-66	60.50	5.92	60.40	6.02

TABLE 2. Wavenumber Assignment (cm^{-1}) of Keto and Enol Bands of Substituted Aryl Acetoacetates in Chloroform

Aryl Group	Ester C=0	Ketone C=0	Ester C=0	Enol C=C
Naphthyl	1764	1720	1649	1627
3-Dimethoxyphenyl	1764	1719	1673	1609
Phenyl-*p*-cresyl	1759	1723	1668	1629
4,6-Trimethylphenyl	1757	1723	1667	1630
Tolyl	1750	1718	1666	1614
Naphthyl	1741	1717	1659	1630
Nitrophenyl	1738	1715	1650	1616
henyl	1737	1716	1630	1603
Methoxyphenyl	1734	1713	1637	1603

ol carbon-carbon double bond 630-1603 cm^{-1}) is in accordance th the work of Rasmussen and rattain (1949) and Leonard *et al.* 952).

Frequencies due to the ester carnyl group vary over a range of cm^{-1}. The highest frequencies e exhibited by compounds possing ortho groups on the aryl oup suggestive of a steric effect, owever the one exception, alphaenyl-*p*-cresyl ester, argues against steric effect. The keto carbonyl nge of values is only 10 cm^{-1}, not nexpected because of the distance tween the keto and ester groups. The trend of the keto carbonyl equencies, excluding the first two lues, parallels that of the ester rbonyl although the significance lessened because of the closeness the estimated error of ± 3 cm^{-1} r each frequency. The enol ester rbonyl bands vary by the greatest nount, 43 cm^{-1}, and parallel close the ester carbonyl frequencies with the glaring exception of alpha-naphthyl and the lesser exception of *p*-methoxyphenyl. Enol carbon-carbon double bond frequencies vary by 27 cm^{-1} and no parallel exists with any of the other three frequency types.

Although alkyl acetoacetates have ultraviolet maxima which, in alcoholic solution, vary little from 240 nm (Korte and Wusten, 1961), the aryl acetoacetates have maxima, as shown in Table 3, which exhibit a wide range of values. The shift toward 220 nm is interesting for it is near 210 nm that alpha-beta unsaturated esters absorb; addition of a hydroxy group on the beta carbon gives the large bathochromic shift to about 240 nm for alkyl acetoacetates (Filler and Naqvi, 1963). All the aryl acetoacetates reported here absorb at a lesser wavelength than alkyl except for the 2,4,6-trimethylphenyl which has a maximum about equal to that of ethyl acetoacetate. Three of the

TABLE 3. Ultraviolet Absorption Maxima of Substituted Aryl Acetoacetates in Absolute Ethanol

Aryl Group	Maxima (nm)	a_m
4,6-Trimethylphenyl	243	1200
a-Naphthyl	236	2200
p-Nitrophenyl	232	760
B-Naphthyl	229	1300
p-Methoxyphenyl	228	6000
p-Tolyl	225	1600
Phenyl	223	840
2,6-Dimethoxyphenyl	220	2400

esters are p-substituted phenyl compounds with the most electron withdrawing member having the highest value and decreasing for p-methoxy groups, although both are higher than the unsubstituted phenyl. The bulky 2,4,6-trimethylphenyl ester absorbs at the highest wavelength with the less bulky alpha-naphthyl ester following. A steric effect suggested by these two groups is countered by the effect of the 2,6-dimethoxyphenyl ester which has the lowest absorption maxima. However, the electronic effect of two *o*-methoxy groups may be important.

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