ultraviolet absorption spectra. The saturated hydrocarbon, presumably ethane, which was found in the exit gases apparently was formed by a reduction of ethylene with concomitant dehydrogenation of other substances in the reaction mixture.[4a]

Experimental

Reaction of Decalin and Ethylene.—To a three-necked flask fitted with a sealed stirrer, condenser and an inlet tube which reached almost to the bottom of the flask was added from 2 to 5 moles of decalin. Ethylene (Matheson Company, 95% pure), which had been washed with 25% sodium hydroxide and 95% sulfuric acid, was added until the decalin was saturated. After the addition of from 0.11 to 0.43 mole of anhydrous aluminum chloride, 1.0 to 1.5 moles of ethylene was added over a period of from seven to twelve hours at an approximately constant rate. The temperature was maintained at 50–60° throughout the reaction. The flow of ethylene was stopped for five minutes of each hour and dry hydrogen chloride was added to reactivate the catalyst. At three-hour intervals, portions of approximately one-third the initial amount of aluminum chloride were added. In the one experiment where the exit gases were collected, the rate of collection increased as the activity of the catalyst decreased.

When stirring was stopped, the mixture separated into two layers: an upper straw colored layer and a pasty reddish-brown catalyst layer. The mixture was poured onto crushed ice and hydrochloric acid. The organic layer was dried over sodium sulfate after being washed with three portions of 6 *N* hydrochloric acid and three portions of water. After removing most of the unreacted decalin through a small packed column, the residue was fractionally distilled through a 60-cm. heated column with a wire spiral packing similar to one described by Cheronis.[6] The amounts of materials actually employed and the fractions obtained by distillation for a typical run are given in Table I.

TABLE I

ALKYLATION OF DECALIN WITH ETHYLENE. A.

Reagents used were 276.5 g. (2 moles) of decalin, 23.5 g. (0.171 mole) of anhydrous aluminum chloride (14.5 g. was added at the start of the reaction), and 28.0 g. (1 mole) of ethylene added during seven and one-half hours. Approximately 3200 cc. of exit gases were collected. Distillation fractions after removal of unreacted decalin were:

Fraction	Weight, g.	B. p., °C. (748 mm.)	n^{25}_{D}
1	1.9	200–203	1.4710
2	1.4	203–207	1.4716
3	1.4	207–208	1.4717
4	3.2	209–212	1.4713
5	3.0	212–215	1.4705
6	4.5	215–220	1.4699
7	2.5	220–221	1.4691
8	1.6	221–222	1.4691
9	1.7	222	1.4691
10	5.8	Residue	1.4700

Analysis of Fractions 7 and 8, Table I.—Fractions 7 and 8 of Table I were combined and a 2.7-g. sample was dehydrogenated by the vapor phase method of Linstead and co-workers[5] at a temperature of 365–375°. Two passes were made over the catalyst and a total of 59% of the theoretical amount of hydrogen and 1.5 g. of pale yellow oil were obtained. A 0.5-g. sample of the oil was dissolved in absolute alcohol and treated with 0.57 g. of picric acid in hot absolute alcohol. A yellow complex precipitated which gave yellow needles which melted at 74–78° after four recrystallizations from methyl alcohol. A mixture with the picric acid complex of known 2-ethyl-naphthalene (m. p. 77–78°) melted at 76–78°. A 1,3,5-trinitrobenzene complex formed in the same manner and recrystallized from methyl alcohol had a melting point of 85.5–86.0°. After mixing with the 1,3,5-trinitrobenzene complex of 2-ethylnaphthalene (m. p. 87.5°), the melting point was 87°.

Analysis of Fraction 10, Table I.—Addition of 0.5 g. of the oil to saturated solutions of picric acid and 1,3,5-trinitrobenzene in absolute alcohol gave an orange color and a yellow color, respectively. These color changes did not occur when decalin or 1- or 2-ethyldecalin was added to alcoholic solutions of the nitro compounds.

Using a Model DU Beckman Spectrophotometer with a 1.000 mm. cell, a solution of 1.2 g. of Fraction (10), Table I in 1 liter of purified cyclohexane gave a broad absorption maximum in the region 260–275 mμ (optical density approximately 0.500 to 0.600).

Analysis of the Exit Gases.—A 2770-cc. sample of the exit gas was shaken with saturated bromine water to remove unreacted ethylene. Analysis of the residual gas (730 cc.) in a modified Orsat gas analysis apparatus showed 3.25% of combustible material. The percentage of combustible material in the original exit gas was calculated to be 0.96%.

UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS
RECEIVED JUNE 25, 1949

---

[6] Cheronis, "Semimicro and Macro Organic Chemistry," Thomas Y. Crowell Company, New York, N. Y., 1942, pp. 74–75.

Steric Effects in the Ultraviolet Absorption Spectra of 2,4,6-Trimethylbenzoic Acid and Methyl Ester

BY EDWARD A. FEHNEL

In connection with our studies of the spectra of substituted phenyl sulfones,[1] it seemed desirable to have available for comparison the spectra of certain substituted benzoic acids, particularly *o*-substituted derivatives in which steric strain might be expected to modify the benzene–carboxyl group interaction. Although the effects of steric inhibition of resonance on the ultraviolet absorption spectra of *o*-dialkyl ketones,[2] anilines,[3] nitrobenzenes,[4] phenols,[5] phenyl ethers,[6] and phenyl sulfides[7] have been investigated, no spectroscopic data seem to have been reported previously for *o*-dialkyl benzoic acids or esters. The ultraviolet spectra of several chlorobenzoic acids have recently been described by Ross,[8] who attributes the decreased absorption observed in the case of the *o*-dichloro acids to suppression of the resonance interaction between the carboxyl group and the benzene ring. The absorption spectra of 2,4,6-trimethylbenzoic acid and methyl 2,4,6-trimethylbenzoate have now been determined and are likewise found to exhibit the expected modifications due to steric effects.

The spectra of benzoic acid and its 2,4,6-trimethyl derivative in ethanol and in 0.01 *N* sodium

---

[1] Fehnel and Carmack, THIS JOURNAL, **72**, 1292 (1950).

[2] O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).

[3] Remington, *ibid.*, **67**, 1838 (1945); Klevens and Platt, *ibid.*, **71**, 1714 (1949).

[4] Brown and Reagan, *ibid.*, **69**, 1032 (1947).

[5] Coggeshall and Lang, *ibid.*, **70**, 3283 (1948).

[6] Fehnel and Carmack, *ibid.*, **71**, 2932 (1949).

[7] Fehnel and Carmack, *ibid.*, **71**, 2889 (1949).

[8] Ross, *ibid.*, **70**, 4039 (1948).

ethoxide are compared in Figs 1 and 2. In both pairs of curves the steric inhibition of the benzene–carboxyl group interaction by the *o*-methyl substituents is indicated by the characteristic suppression of the long wave length absorption maxima and the hypsochromic displacement of the short wave length band. The shift of both curves toward shorter wave lengths and lower intensities in the alkaline medium is in accord with the observations of other investigators on related compounds,[9] and is attributed to the less electrophilic character of the negatively charged carboxylate group as compared with the uncharged carboxyl group. The spectra of methyl benzoate and methyl 2,4,6-trimethylbenzoate in ethanol (Table I) are almost identical with those of the corresponding acids in the same solvent.

Experimental

The ultraviolet absorption measurements were made as described in a previous paper.[10] Benzoic acid (J. T. Baker C. P., resublimed) was recrystallized from water before use; m. p. 121–121.5°. Methyl benzoate (Eastman Kodak Co.) was redistilled and a portion of the middle fraction, b. p. 197°, was taken for determination of the spectrum. 2,4,6-Trimethylbenzoic acid, m. p. 152–153° after two recrystallizations from petroleum ether, was prepared by carbonation of mesitylmagnesium bromide according to the directions given by Barnes.[11] The methyl ester, which was prepared from the acid by the method of Newman,[12] was distilled twice and a portion of the middle fraction from the second distillation, b. p. 131° at 35 mm., was taken for determination of the spectrum. The wave lengths and molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	Solvent[a]	Maxima[b]	
		λ (mμ)	ε
2,4,6-Trimethylbenzoic acid	EtOH	(270)	420
		(235)	3270
		<215	>10000
2,4,6-Trimethylbenzoic acid	NaOEt	269	310
		<215	>8000
Methyl 2,4,6-trimethylbenzoate	EtOH	273	490
		(235)	3910
		<215	>10000
Benzoic acid[c]	EtOH	279	690
		272	840
		227	10470
Benzoic acid[c]	NaOEt	269	590
		262	620
		222	8830
Methyl benzoate	EtOH	280	720
		272	880
		228	11800

[a] EtOH designates absolute ethanol; NaOEt designates 0.01 *N* sodium ethoxide prepared by dissolving sodium in absolute ethanol. [b] The wave lengths in parentheses refer to inflection points. [c] *Cf.* Kumler and Strait, THIS JOURNAL, **65**, 2349 (1943); Doub and Vandenbelt, *ibid.*, **69**, 2714 (1947).

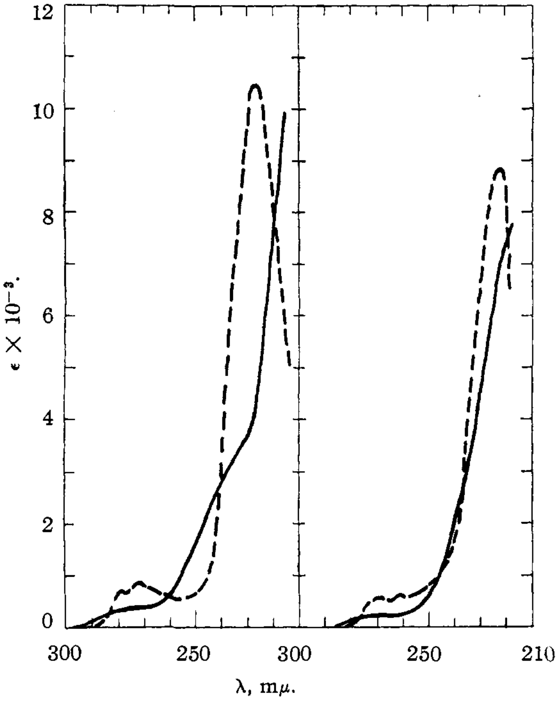

Fig. 1. Fig. 2.

Fig. 1.—Absorption spectra of 2,4,6-trimethylbenzoic acid, ——, and benzoic acid, – – – – –; solvent, EtOH.

Fig. 2.—Absorption spectra of 2,4,6,-trimethylbenzoic acid, ——, and benzoic acid, – – – – –; solvent, 0.01 *N* NaOEt.

DEPARTMENT OF CHEMISTRY
SWARTHMORE COLLEGE
SWARTHMORE, PA.

RECEIVED AUGUST 25, 1949

---

[9] See, for example, Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); *ibid.*, **71**, 2414 (1949).

[10] Fehnel and Carmack, *ibid.*, **71**, 84 (1949).

[11] Barnes, *Organic Syntheses*, **21**, 77 (1941).

[12] Newman, THIS JOURNAL, **63**, 2431 (1941).

Some Mercaptols of Simple Cyclic Ketones

BY H. HAUPTMANN AND M. MOURA CAMPOS

While studying steroid mercaptols one of us[1] noted distinct differences in the reactivity of keto groups toward mono- and dithiols. It seemed worth while to apply the same reactions to some simple cyclic ketones in order to see whether or not the same differences could be noted. Therefore, cyclohexanone, menthone and camphor were allowed to react with benzylmercaptan, ethanedithiol and propane-1,3-dithiol.

Two different kinds of condensing agents are commonly employed for mercaptol formation. One is a mixture of anhydrous zinc chloride and anhydrous sodium sulfate,[2] the other is gaseous hydrogen chloride.[3] Each has been examined in

---

[1] H. Hauptmann, THIS JOURNAL, **69**, 562 (1947).

[2] E. Baumann, *Ber.*, **19**, 2083 (1886); M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **66**, 909 (1944).

[3] E. Baumann, *Ber.*, **18**, 263 (1885).