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).

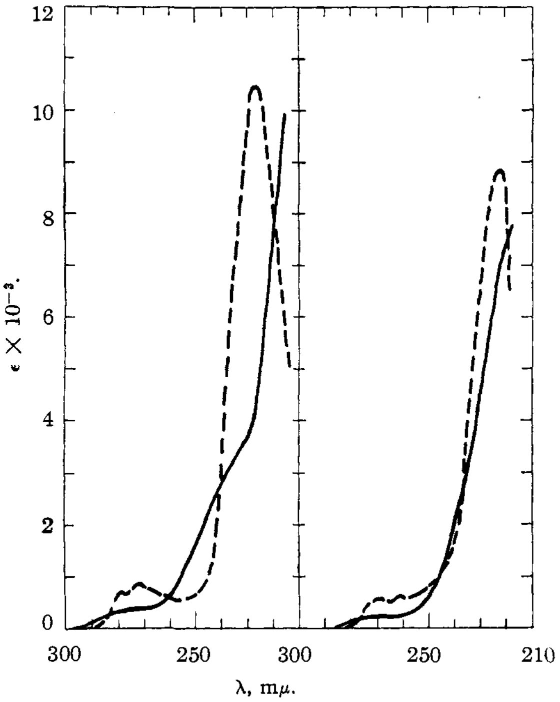

Fig. 1. Fig. 2.

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.

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[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

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

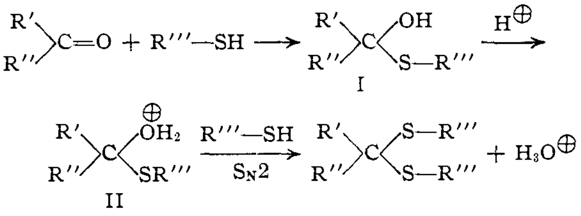
[2] E. Baumann, *Ber.*, **19**, 2083 (1886); M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **66**, 909 (1944).

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

our laboratory and we have concluded that hydrogen chloride is the more active since camphor ethylenemercaptol is obtained in its presence but not by means of the other method. An analogous observation was made during the preparation of ethyl dehydrocholate triethylenemercaptol which could be obtained only in the presence of hydrogen chloride.[1]

The experimental results show that camphor forms mercaptols with dithiols but not with monothiols. There is a sharp difference in reactivity between camphor, on one hand, and cyclohexanone and menthone on the other. These latter form mercaptols with either benzyl mercaptan or dimercaptans.[4]

In passing from cyclohexanone through menthone to camphor there is increased steric hindrance about the carbonyl group. Mercaptol formation probably occurs through the intermediate formation of a hemimercaptol (I). In the presence of an acid catalyst I forms a new cation (II) which now undergoes an S_N2 attack by a second thiol grouping. This latter reaction is markedly slowed down by the steric effects of groups R′ and R″ when the reaction is bimolecular. However, intramolecular reactions are not markedly affected by such steric hindrance and, therefore, a mercaptol formation involving a dithiol of the type $HS-(CH_2)_n-SH$ (where n = 2 or 3) leading to a five- or six-membered ring is rapid.



In consequence of the cage structure in camphor the S_N2 reaction is especially hindered in the simple bimolecular case, but is much less affected in the intramolecular reaction involving dithiols.

A similar situation is to be found with the 7- and 12-ketosteroids which also have considerable hindrance around the carbonyl groups.[5]

Experimental

Cyclohexanone Ethylenemercaptol.—Six and six-tenths grams of $(NH_4)_3ZnCl_5$ was heated in a current of dry hydrogen chloride until the formation of gaseous products was finished. After cooling, 3 g. of anhydrous sodium sulfate, 5 g. of cyclohexanone (0.05 mole) and 7.5 g. of ethanedithiol (0.075 mole) were added to the fused residue of zinc chloride. After standing at room temperature for one day, the mixture was heated in a water-bath for two hours and then extracted with ether. The ethereal solution was washed with 5% sodium hydroxide solution and dried with calcium chloride. Then the ether was evaporated and the oily residue fractionated at reduced pressure. A colorless liquid (5.3 g.) distilled at 114–115° (6 mm.), yield 60%.

Anal. Calcd. for $C_8H_{14}S_2$: S, 36.78. Found: S, 36.49.

Cyclohexanone Trimethylenemercaptol.—Cyclohexanone (4.8 g., 0.05 mole) and 8 g. (0.08 mole) of propane-1,3-dithiol when treated as described before yielded an oil which, after distillation at 148–148.5° (17 mm.), crystallized from ethanol; m. p. 40.5–41.5°, yield 7.5 g. (79%).

Anal. Calcd. for $C_9H_{16}S_2$: S, 34.04. Found: S, 33.92.

Menthone Ethylenemercaptol.—Menthone (5 g., 0.032 mole) and 3.5 g. of ethanedithiol (0.038 mole) when treated as described before formed an oil which distilled at 113–115° (3.5 mm.), yield 3.5 g. (48%).

Anal. Calcd. for $C_{12}H_{22}S_2$: S, 27.84. Found: S, 27.64.

Menthone Trimethylenemercaptol.—A mixture of 7.2 g. of menthone (0.046 mole) and 5.2 g. of propane-1,3-dithiol (0.047 mole) was cooled in an ice-bath and a stream of hydrogen chloride passed through the solution for two hours. After this time the mixture was quite turbid. Excess hydrogen chloride was removed in a vacuum desiccator over sodium hydroxide and the mixture dissolved in ether, washed with 5% sodium hydroxide and water and dried with calcium chloride. The ether was distilled off and the remaining oil distilled off *in vacuo*, b. p. 152–155° (3 mm.). The distillate solidified and could be recrystallized from ethanol; m. p. 41–42°, yield 6.5 g. (58%).

Anal. Calcd. for $C_{13}H_{24}S_2$: S, 26.25. Found: S, 26.05.

Menthone Dibenzylmercaptol.—Menthone (5 g., 0.032 mole) and 8.7 g. of benzylmercaptan (0.07 mole) when treated as described for menthone trimethylenemercaptol formed 3.8 g. of colorless crystals; m. p. 81–82.5°, yield 30%.

Anal. Calcd. for $C_{24}H_{32}S_2$: S, 16.68. Found: S, 16.82.

Cyclohexanone Dibenzylmercaptol.—Cyclohexanone (2.5 g., 0.025 mole) and 6.2 g. of benzylmercaptan (0.05 mole) when treated in the same manner yielded 6.4 g. of an oil; b. p. 165–167° (0.05 mm.), yield 3.5 g. (42%).

Anal. Calcd. for $C_{20}H_{24}S_2$: S, 19.54. Found: S, 19.29, 19.30.

Camphor Ethylenemercaptol.—Camphor (6.4 g., 0.042 mole) and 4.4 g. of ethanedithiol (0.047 mole) when treated in the same manner yielded 4.8 g. (45%) of an oil, b. p. 108–110° (5 mm.).

Anal. Calcd. for $C_{12}H_{20}S_2$: S, 28.07. Found: S, 27.90.

When treated as described for cyclohexanone ethylenemercaptol, no mercaptol formation was observed and the camphor was recovered.

Camphor Trimethylenemercaptol.—Camphor (9.8 g., 0.064 mole) and propane-1,3-dithiol (7.7 g., 0.07 mole) when treated as described for menthone trimethylenemercaptol yielded 8 g. (50%) of an oil, b. p. 140–143° (4 mm.).

Anal. Calcd. for $C_{13}H_{22}S_2$: S, 26.45. Found: S, 26.18.

Camphor Dibenzylmercaptol.—No mercaptol was obtained when camphor (2 g., 0.013 mole) and 3.2 g. of benzylmercaptan (0.026 mole) were treated in the same manner. Although the mixture became slightly turbid, the camphor was recovered.

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[4] With ethanethiol no mercaptol could be isolated using either menthone or camphor. It seems that with menthone the mercaptol is formed but is decomposed on distillation. This behavior is reported for cyclohexanone diethylmercaptol by A. Rezsei, *Ber.*, **60**, 1420 (1947).

[5] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 125.