Substituted Picrates of Hydrocarbons and Amines. II.

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Chloro-, bromo-, iodo-, *tert*-butyl, and methoxypicric acids were shown to form complexes with aromatic hydrocarbons and to form salts with amines. Some salts and complexes could not be isolated, but in many cases their formation was shown by means of phase diagrams.

PREVIOUS WORK by the present investigators has dealt with the effects of small alkyl substituents in the 3- and 3,5-positions of picric acid (*4*).

This investigation deals with some of the properties of the halo picric acids, *tert*-butylpicric acid and methoxypicric acid. These acids were chosen to provide a greater variety of inductive and steric factors and to test whether those groups would significantly alter the complexing ability and salt formation ability of picric acid.

The five picric acids used in this work are well known compounds (*1–3, 6*), but with the exception of pyridine and quinoline methoxypicrates (*1*) none of their complexes nor amine salts have been reported.

An attempt to synthesize fluoropicric acid following the method of Hodgson and Nixon (*3*) led to styphnic acid. It seems probable Hodgson and Nixon also isolated styphnic acid since the melting point of their product was reported as only four degrees lower than that of styphnic acid. These authors (*3*) reported a nitrogen analysis which would fit either fluoropicric acid or styphnic acid.

The following amines were selected for reaction with the picric acids: 2-picoline, pyridine, *N,N*-dimethylaniline, *N*-methylaniline, quinoline, aniline, *m*-nitroaniline, *p*-nitroaniline, and *o*-nitroaniline. These amines ranged in pK_b values from 2.87 to 13.84. Naphthalene, anthracene, and hexamethylbenzene were chosen as aromatic hydrocarbons for complex formation.

Table I lists the melting points and nitrogen analyses of the stable compounds formed in the reactions of the substituted picric acids with amines and aromatic hydrocarbons. In cases where stable compounds could not be isolated, phase diagrams (*4*) of the two component systems were determined as a criterion of compound formation. Table II lists the melting points as indicated by compound formation maxima from the phase diagrams.

All the picric acids used in this work reacted with the bases to form characteristic yellow salts. The only stable, isolable, aromatic hydrocarbon complexes were those formed in the reaction of hexamethylbenzene with chloropicric acid and bromopicric acid.

Table I. 3-Substituted Picrates of Amines

Compound	Formula	Recrystallization Solvent	Color	M.P.	Nitrogen, % Calcd.	Nitrogen, % Found
Piperidine chloropicrate	$C_{11}H_{11}N_4O_7Cl$	Abs. Ethanol	Yellow	174–175d.	16.11	15.89
2-Picoline chloropicrate	$C_{12}H_9N_4O_7Cl$	Abs. Ethanol	Yellow	194–195d.	15.75	15.58
Pyridine chloropicrate	$C_{11}H_7N_4O_7Cl$	Abs. Ethanol	Yellow	161–162d.[a]	16.40	16.38
N,N-Dimethylaniline chloropicrate	$C_{14}H_{13}N_4O_7Cl$	Abs. Ethanol	Yellow	187–188d.	14.60	14.43
N-Methylaniline chloropicrate	$C_{13}H_{11}N_4O_7Cl$	Abs. Ethanol	Yellow	165–166d.	15.15	15.12
Quinoline chloropicrate	$C_{15}H_9N_4O_7Cl$	Abs. Ethanol	Yellow	226–227d.	14.30	14.20
Piperidine bromopicrate	$C_{11}H_{11}N_4O_7Br$	Abs. Ethanol	Yellow	174–175d.	14.25	14.16
2-Picoline bromopicrate	$C_{12}H_9N_4O_7Br$	Abs. Ethanol	Yellow	219–220d.	13.97	13.85
Pyridine bromopicrate	$C_{11}H_7N_4O_7Br$	Abs. Ethanol	Yellow	170–171d.[a]	14.47	14.16
N,N-Dimethylaniline bromopicrate	$C_{14}H_{13}N_4O_7Br$	Abs. Ethanol	Yellow	191–192d.	13.05	13.19
N-Methylaniline bromopicrate	$C_{13}H_{11}N_4O_7Br$	Abs. Ethanol	Yellow	171–172d.	13.50	13.63
Quinoline bromopicrate	$C_{15}H_9N_4O_7Br$	Abs. Ethanol	Yellow	243–244d.	12.82	12.60
Piperidine iodopicrate	$C_{11}H_{11}N_4O_7I$	Abs. Ethanol	Yellow	193–194d.	12.73	12.90
2-Picoline iodopicrate	$C_{12}H_9N_4O_7I$	Abs. Ethanol	Yellow	222–223d.	12.50	12.34
Pyridine iodopicrate	$C_{11}H_7N_4O_7I$	Abs. Ethanol	Yellow	189–190d.	12.91	12.79
N,N-Dimethylaniline iodopicrate	$C_{14}H_{13}N_4O_7I$	Abs. Ethanol	Yellow	184–185d.	11.77	11.74
N-Methylaniline iodopicrate	$C_{13}H_{11}N_4O_7I$	Abs. Ethanol	Yellow	158–159d.	12.12	11.92
Quinoline iodopicrate	$C_{15}H_9N_4O_7I$	Abs. Ethanol	Yellow	252–253d.	11.57	11.43
Piperidine *tert*-butylpicrate	$C_{15}H_{20}N_4O_7$	Ethanol	Yellow	171–172d.	15.13	15.06
2-Picoline *tert*-butylpicrate	$C_{16}H_{18}N_4O_7$	Ethanol	Yellow	138–139d.	14.81	14.72
Pyridine *tert*-butylpicrate	$C_{15}H_{16}N_4O_7$	Ethanol	Yellow	177–178d.	15.37	15.19
N,N-Dimethylaniline *tert*-butylpicrate	$C_{18}H_{22}N_4O_7$	Ethanol	Yellow	109–110d.	13.79	13.93
Quinoline *tert*-butylpicrate	$C_{19}H_{18}N_4O_7$	Ethanol	Yellow	192–193d.	13.52	13.37
Piperidine methoxypicrate	$C_{12}H_{14}N_4O_8$	Methanol	Yellow	166–167d.	16.27	16.05
2-Picoline methoxypicrate	$C_{13}H_{12}N_4O_8$	Methanol	Yellow	161–162d.	15.91	15.78
Pyridine methoxypicrate	$C_{12}H_{10}N_4O_8$	Methanol	Yellow	150–151d.[b]	16.57	16.28
N,N-Dimethylaniline methoxypicrate	$C_{15}H_{16}N_4O_8$	Methanol	Yellow	153–154d.	14.73	14.84
Quinoline methoxypicrate	$C_{16}H_{12}N_4O_8$	Methanol	Yellow	180–181d.[c]	14.43	14.39
Aniline methoxypicrate	$C_{13}H_{12}N_4O_8$	Methanol	Yellow	161–162d.	15.91	16.07
m-Nitroaniline methoxypicrate	$C_{13}H_{11}N_5O_{10}$	Ethanol	Yellow	123–124d.	17.63	17.80
p-Nitroaniline methoxypicrate	$C_{13}H_{11}N_5O_{10}$	Ethanol	Yellow	103–104d.	17.63	17.47

[a] Resolidifies within two degrees, decomposes above 200°.
[b] Reported 140–145°, M. Kohn and G. Loff, *Monatsh* **45**, 605 (1925).
[c] Reported 165–175°, *ibid.*

Table II. Phase Diagram Maxima

Compound	M.P.[a]
o-nitroaniline chloropicrate	100°
naphthalene chloropicrate	128°
anthracene chloropicrate	152°
naphthalene bromopicrate	113°
anthracene bromopicrate	184°
anthracene iodopicrate	164°
m-nitroaniline *tert*-butylpicrate	156°
p-nitroaniline *tert*-butylpicrate	147°
naphthalene *tert*-butylpicrate	133°
anthracene *tert*-butylpicrate	183°
hexamethylbenzene *tert*-butylpicrate	149°
naphthalene methoxypicrate	78°
anthracene methoxypicrate	188°
hexamethylbenzene methoxypicrate	139° (1:2)
hexamethylbenzene methoxypicrate	120° (2:1)

[a] M.P. are taken from maxima of phase diagrams indicating 1:1 compound formation except as indicated.

The infrared spectra of all isolable compounds in this research were determined and found to be very similar to those previously reported (*4*).

EXPERIMENTAL

Microanalyses were by Microtech Laboratories, Skokie, Ill. All infrared spectra were recorded on a Perkin-Elmer, Model 21, spectrophotometer using nujol mulls.

Preparation of picric acids: chloro-, bromo-, and iodopicric acids were prepared by the method of Hodgson and coworkers (*2*, *3*). The preparation of *m*-*tert*-butylphenol followed the method of Carpenter (*1*). Nitration of this phenol was done by the method of Moore (*5*).

The nitration of *m*-fluorophenol followed the method of Hodgson and Nixon (*3*). Recrystallization of the solid, using water as a solvent, gave light yellow crystals, m.p. 168–172°. The infrared spectrum of this material closely matched that of an authentic sample of styphnic acid and a mixed melting point of this material with styphnic acid showed no depression.

Methoxypicric acid was prepared by nitrating *m*-methoxyphenol by the method of Moore (*5*).

The methods used in the preparation of the 3-substituted picrates of hydrocarbons and amines, the melting points of these compounds, and the phase diagrams have been previously described (*4*).

Hexamethylbenzene chloropicrate and bromopicrate were obtained analytically pure from the reaction mixture and did not require recrystallization. Hexamethylbenzene chloropicrate: orange crystals (m.p. 146–148°d). *Anal:* Calc. for $C_{18}H_{20}N_3O_7Cl$: 9.86%N; Found 9.75%N. Hexamethylbenzene bromopicrate: orange crystals (m.p. 148–150° d). *Anal:* Calcd. for $C_{18}N_{20}N_3O_7Br$: 8.93%N; Found 9.08%N.

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Synthesis of 3-Hydroxy-4-methoxybutyrophenone

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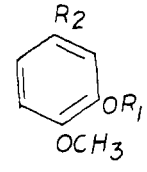
Friedel-Crafts condensation of guaiacol with butyric anhydrides using a phosphoric acid catalyst produces 3-butyroxy-4-methoxybutyrophenone whereas condensation using aluminum chloride or polyphosphoric acid catalysts produces 3-methoxy-4-hydroxybutyrophenone. A possible explanation of the unique nature of phosphoric acid is offered.

ALTHOUGH A NUMBER of ketonic derivatives of guaiacol have been prepared by Friedel-Crafts acylation, the side chain introduced by the acylation normally is directed para to the phenolic group (*4*, *5*) rather than para to the methoxyl group (*6*). The acylation probably proceeds by way of a Fries rearrangement of the phenolic ester formed initially (*1*). We were interested in introducing an acyl group para to the methoxyl group in guaiacol, and have synthesized one such compound, 3-hydroxy-4-methoxybutyrophenone (I). Acylation of guaiacol with butyric anhydride and syrupy phosphoric acid yielded a mixture of guaiacol butyrate (II) and 3-butyroxy-4-methoxybutyrophenone (III). The latter compound was hydrolyzed to I with sodium methoxide in methanol.



I. $R_1 = H$, $R_2 = COCH_2CH_2CH_3$
II. $R_1 = COCH_2CH_2CH_3$, $R_2 = H$
III. $R_1 = COCH_2CH_2CH_3$, $R_2 = COCH_2CH_2CH_3$
IV. $R_1 = H$, $R_2 = COC(=NOH)CH_2CH_3$
V. $R_1 = COCH_3$, $R_2 = COC(=NOCOCH_3)CH_2CH_3$

Friedel-Crafts acylation of guaiacol with aluminum chloride or with polyphosphoric acid directed the butyryl