[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LOYOLA UNIVERSITY OF CHICAGO]

Alkyl-Substituted Picrates of Hydrocarbons and Amines[1]

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Received November 17, 1960

Methyl-, ethyl-, and dimethylpicric acids were shown to form complexes with a variety of aromatic hydrocarbons. Some complexes could not be isolated, but their formation was proved by means of phase diagrams. The substituted picric acids also formed salts with various amines. The infrared spectra of the amine picrates are reported. The picrates of carbazole are true complexes and not salts.

The properties of picric acids having alkyl-substituents at the 3- and 3,5- positions have been studied by Moore,[4,5] who was especially interested in their selectivity in the precipitation of metal ions. The effects of these substitutions on the reagent involve several factors which are not entirely independent of one another. The present work is concerned with the reactions and properties of 3-methyl-, 3-ethyl-, and 3,5-dimethylpicric acids as precipitating agents for various aromatic hydrocarbons and amines.

In the case of methylpicric acid, it was interesting to note that, with all the eight aromatic hydrocarbons, *pi* complexes could be isolated in every case, showing that complexing ability was not affected. The steric factor is very probably the reason why no *pi* complexes could be isolated in the reaction of anthracene, fluorene and hexamethylbenzene with ethylpicric acid. It was possible to isolate the *pi* complexes of the other five aromatic hydrocarbons with ethylpicric acid. When dimethylpicric acid was used, it was not possible to isolate any of the *pi* complexes of the eight aromatic hydrocarbons studied here.

By preparing various mole-percent mixtures of the hydrocarbons and the substituted picric acids and determining the melting point range and so the phase diagrams for the various systems (Figs. 1–6), it was found that a substituted picrate of *every* hydrocarbon studied here was indeed formed. Apparently, eleven of them were so unstable that they dissociated with great ease and so could not be isolated.

In every case, except for that of fluorene, the phase diagrams indicated 1:1 complexes were formed. In the case of the two fluorene complexes, as shown by the phase diagrams, the mole ratio is two substituted picric acids for each molecule of fluorene. Also, the phase diagrams of hexamethylbenzene and phenanthrene with dimethylpicric acid indicated the presence of a metastable state. It would seem, therefore, that the substituted picric acids still possess complexing ability, but that this is greatly diminished as steric factors become more prominent.

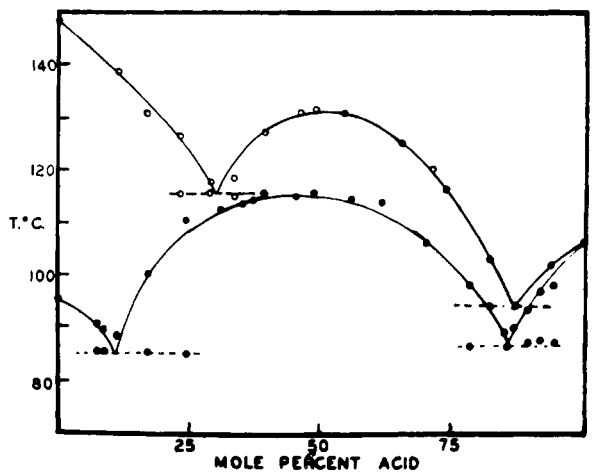

Fig. 1. Upper curve, pyrene and dimethylpicric acid; lower curve, acenaphthene and dimethylpicric acid

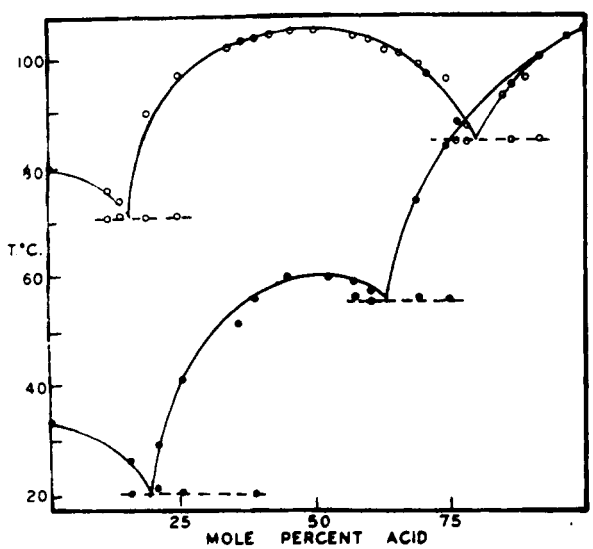

Fig. 2. Upper curve, naphthalene and dimethylpicric acid; lower curve, 2-methylnaphthalene and dimethylpicric acid

(1) Presented before the Division of Organic Chemistry at the Cleveland Meeting of the American Chemical Society in April, 1960.

(2) Taken in part from the Master of Science thesis of M. J. Gruber.

(3) National Science Foundation Fellow, 1958–1960. Taken in part from the Master of Science thesis of J. W. Elder, S.J.

(4) C. E. Moore and R. Peck, *J. Org. Chem.*, **20**, 673 (1955).

(5) C. E. Moore, M. Lally, R. Anderson, J. Brady, and R. McLafferty, *Anal. Chim. Acta*, **15**, 1 (1956).

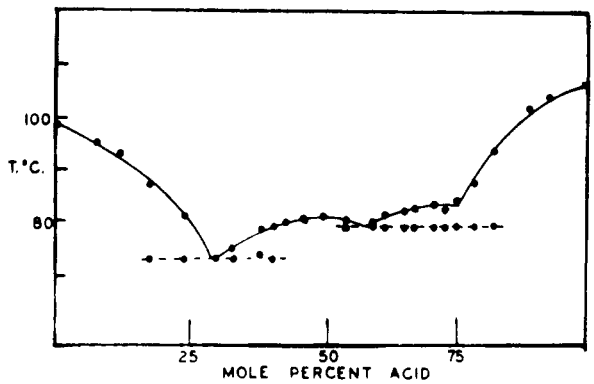

Fig. 3. Phenanthrene and dimethylpicric acid

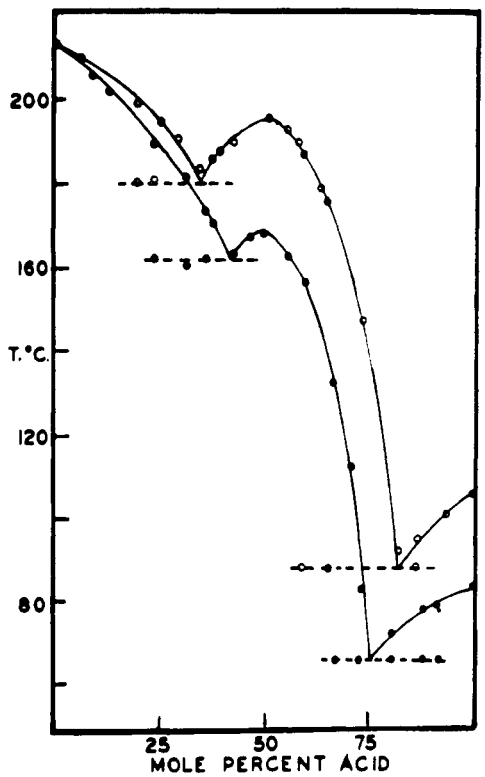

Fig. 4. Upper curve, anthracene and dimethylpicric acid; lower curve, anthracene and ethylpicric acid

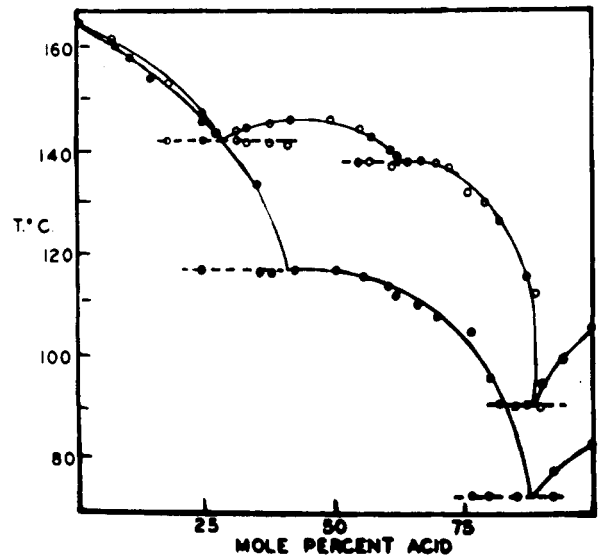

Fig. 5. Upper curve, hexamethylbenzene and dimethylpicric acid; lower curve, hexamethylbenzene and ethylpicric acid

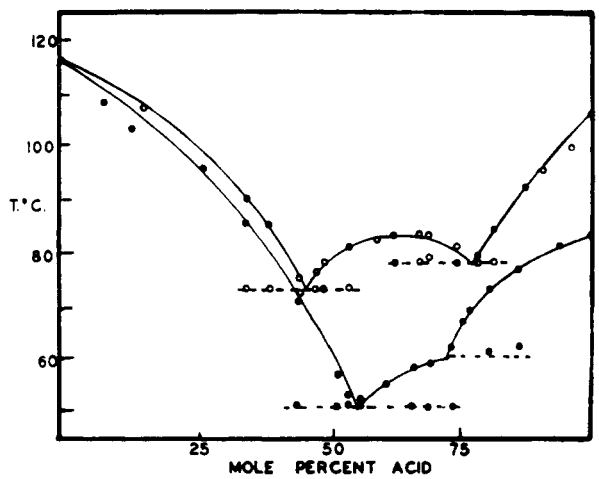

Fig. 6. Upper curve, fluorene and dimethylpicric acid; lower curve, fluorene and ethylpicric acid

Acidity factor. Another important property of picric acid is its acidity. Because of resonance between the three nitro groups and the aromatic ring, the acidity of the phenolic hydrogen is greatly enhanced and picric acid is a reasonably strong acid. In the case of the substituted picric acids, the presence of groups in the 3- and 3,5-positions twist the nitro groups out of the plane of the ring, thereby decreasing the resonance interaction and decreasing the acidity. A previous report[4] indicated that the acidity of the alkyl substituted picric acids is lowered (pK$_a$'s in the range of 2.8 to 3.3) as compared to picric acid itself (pK$_a$ of 0.29). An independent communication,[6] using spectrophotometric methods instead of potentiometric methods,[4] indicate that the values may be in the range of 1 to 2.

Picric acid forms salts with many basic amines, and it was interesting to determine whether the substituted picric acids would also form salts as readily. A variety of 17 different amines were selected for this study, and their pK$_b$ values ranged from 2.8 to 14.00. For amines with pK_b values in the range 2.8 to 10.08, yellow salts were readily formed with all the substituted picric acids. As was expected, diphenylamine and triphenylamine did not form any picrates. Carbazole, however, formed orange or red derivatives with picric acid, methylpicric acid, and dimethylpicric acid. As the carbazole picrates were not yellow like the other amine picrates, and from infrared evidence, it was concluded that carbazole picrates were complexes and not true salts.

(6) We are indebted to the National Bureau of Standards or this information.

TABLE I

HYDROCARBON AND AMINE PICRATES

Compound	Formula	Recrystallization Solvent	Recrystallization Solvent	Color	M.P.	Nitrogen, % Calcd.	Nitrogen, % Found
Acenaphthene methylpicrate	$C_{19}H_{15}N_3O_7$	Ethanol	—	Orange	122–123	[a]	—
Anthracene methylpicrate	$C_{21}H_{15}N_3O_7$	Toluene	—	Orange	142–143	9.98	10.13
Fluorene methylpicrate	$C_{20}H_{15}N_3O_7$	Ether	—	Orange	108	[b]	—
Hexamethylbenzene methylpicrate	$C_{19}H_{23}N_3O_7$	Ethanol	—	Yellow	150–151	10.37	10.44
2-Methylnaphthalene methylpicrate	$C_{18}H_{15}N_3O_7$	Ethanol	—	Yellow	115	10.91	10.71
Naphthalene methylpicrate	$C_{17}H_{13}N_3O_7$	Ethanol	—	Yellow	114	[c]	—
Phenanthrene methylpicrate	$C_{21}H_{15}N_3O_7$	Ethanol	—	Yellow	120–121	[d]	—
Pyrene methylpicrate	$C_{23}H_{15}N_3O_7$	Ethanol	—	Orange	162–163	[e]	—
Acenaphthene ethylpicrate	$C_{20}H_{17}N_3O_7$	Benzene	—	Yellow	66	10.22	10.44
2-Methylnaphthalene ethylpicrate	$C_{19}H_{17}N_3O_7$	Ethanol	—	Yellow	42	10.52	10.45
Naphthalene ethylpicrate	$C_{18}H_{15}N_3O_7$	Ethanol	—	Yellow	61–62	10.91	11.14
Phenanthrene ethylpicrate	$C_{22}H_{17}N_3O_7$	Ethanol	—	Orange	95–96	9.66	9.56
Pyrene ethylpicrate	$C_{24}H_{17}N_3O_7$	Ethanol	—	Orange	104–105	9.15	9.05
Ethylamine methylpicrate	$C_9H_{12}N_4O_7$	Methanol	Ethanol	Yellow	188–189 dec.	19.44	19.59
Diethylamine methylpicrate	$C_{11}H_{16}N_4O_7$	Ether	Ether	Yellow	152–153 dec.	17.72	17.65
Triethylamine methylpicrate	$C_{13}H_{20}N_4O_7$	Methanol	Ethanol	Yellow	115–116 dec.	16.27	16.44
Aniline methylpicrate	$C_{13}H_{12}N_4O_7$	Water	Water	Yellow	175–176 dec.	16.37	16.38
N-Methylaniline methylpicrate	$C_{14}H_{14}N_4O_7$	Methanol	Methanol	Yellow	127–128 dec.	16.00	16.05
N,*N*-Dimethylaniline methylpicrate	$C_{15}H_{16}N_4O_7$	Methanol	Methanol	Yellow	177–178 dec.	15.38	15.16
Benzylamine methylpicrate	$C_{14}H_{14}N_4O_7$	Methanol	Methanol	Yellow	198–199 dec.	16.00	15.92
Pyridine methylpicrate	$C_{12}H_{10}N_4O_7$	Methanol	Methanol	Yellow	198–199 dec.	17.39	17.59
2-Picoline methylpicrate	$C_{13}H_{12}N_4O_7$	Methanol	Methanol	Yellow	192–193 dec.	16.66	16.66
2,6-Lutidine methylpicrate	$C_{14}H_{14}N_4O_7$	Methanol	Methanol	Yellow	205–207 dec.	16.00	16.11
Piperidine methylpicrate	$C_{12}H_{16}N_4O_7$	Methanol	Methanol	Yellow	289–290 dec.	17.07	16.88
Morpholine methylpicrate	$C_{11}H_{14}N_4O_8$	Methanol	Methanol	Yellow	234–235 dec.	16.97	16.95
1-Naphthylamine methylpicrate	$C_{17}H_{14}N_4O_7$	Methanol	Methanol	Yellow-green	176–177 dec.	14.50	14.35
Quinoline methylpicrate	$C_{16}H_{12}N_4O_7$	Methanol	Methanol	Yellow	222–223 dec.	15.05	15.03
Carbazole methylpicrate	$C_{19}H_{14}N_4O_7$	Ligroin	—	Orange	157–158 dec.	13.65	13.35
Ethylamine ethylpicrate	$C_{10}H_{14}N_4O_7$	Methanol	Ethanol	Yellow	195–196 dec.	18.54	18.59
Diethylamine ethylpicrate	$C_{12}H_{18}N_4O_7$	Methanol	Ethanol	Yellow	114–115 dec.	16.96	17.25
Triethylamine ethylpicrate	$C_{14}H_{22}N_4O_7$	Methanol	Ethanol	Yellow	84– 85 dec.	15.64	15.69
Aniline ethyl picrate	$C_{14}H_{14}N_4O_7$	Water	Water	Yellow	164–165 dec.	16.00	15.97
N-Methylaniline ethylpicrate	$C_{15}H_{16}N_4O_7$	Methanol	Methanol	Yellow	114–115 dec.	15.38	15.66
N,*N*-Dimethylaniline ethylpicrate	$C_{16}H_{18}N_4O_7$	Methanol	Methanol	Yellow	146–148 dec.	14.81	14.60
Benzylamine ethylpicrate	$C_{15}H_{16}N_4O_7$	Methanol	Methanol	Yellow	167–168 dec.	15.38	15.55
Pyridine ethylpicrate	$C_{13}H_{12}N_4O_7$	Methanol	Methanol	Yellow	182–183 dec.	16.66	16.76
2-Picoline ethylpicrate	$C_{14}H_{14}N_4O_7$	Methanol	Methanol	Yellow	164–165	16.00	15.97
2,6-Lutidine ethylpicrate	$C_{15}H_{16}N_4O_7$	Methanol	Methanol	Yellow	152–153 dec.	15.38	15.42
Piperidine ethylpicrate	$C_{13}H_{18}N_4O_7$	Methanol	Methanol	Yellow	193–194 dec.	16.37	16.31
Morpholine ethylpicrate	$C_{12}H_{16}N_4O_8$	Methanol	Methanol	Yellow	175–176 dec.	16.27	16.35
1-Naphthylamine ethylpicrate	$C_{18}H_{14}N_4O_7$	Ether	Ether	Yellow-green	164–165 dec.	14.07	14.12
Quinoline ethylpicrate	$C_{17}H_{14}N_4O_7$	Methanol	Methanol	Yellow	202–203 dec.	14.50	14.56
Ethylamine dimethylpicrate	$C_{10}H_{14}N_4O_7$	Ethanol	Ethanol	Yellow	237–239 dec.	18.54	18.48
Diethylamine dimethylpicrate	$C_{12}H_{18}N_4O_7$	Ethanol	Ethanol	Yellow	199–200 dec.	16.96	16.86
Triethylamine dimethylpicrate	$C_{14}H_{22}N_4O_7$	Ethanol	Ethanol	Yellow	76– 77 dec.	15.64	15.64
Aniline dimethylpicrate	$C_{14}H_{14}N_4O_7$	Water	Water	Yellow	200–201 dec.	16.00	16.14
N-Methylaniline dimethylpicrate	$C_{15}H_{16}N_4O_7$	Ethanol	Methanol	Yellow	165–166 dec.	15.38	15.32
N,*N*-Dimethylaniline dimethylpicrate	$C_{16}H_{18}N_4O_7$	Ethanol	Methanol	Yellow	110–111 dec.	14.71	14.99
Benzylamine dimethylpicrate	$C_{15}H_{16}N_4O_7$	Ethanol	Methanol	Yellow	230–231 dec.	15.38	15.28
Pyridine dimethylpicrate	$C_{13}H_{12}N_4O_7$	Ethanol	Methanol	Yellow	157–158	16.66	16.43
2-Picoline dimethylpicrate	$C_{14}H_{14}N_4O_7$	Ethanol	Methanol	Yellow	150–151	16.00	16.30
2,6-Lutidine dimethylpicrate	$C_{15}H_{16}N_4O_7$	Ethanol	Methanol	Yellow	164–165	15.38	15.33
Piperidine dimethylpicrate	$C_{13}H_{18}N_4O_7$	Ethanol	Methanol	Yellow	242–243 dec.	16.37	16.30
Morpholine dimethylpicrate	$C_{12}H_{16}N_4O_8$	Ethanol	Methanol	Yellow	255–256 dec.	16.28	16.00
1-Naphthylamine dimethylpicrate	$C_{18}H_{14}N_4O_7$	Ethanol	Ethanol	Yellow-green	163–164 dec.	14.07	13.78
Quinoline dimethylpicrate	$C_{17}H_{14}N_4O_7$	Ethanol	Methanol	Yellow	217–218 dec.	14.50	14.66
Carbazole dimethylpicrate	$C_{20}H_{16}N_4O_7$	Ligroin	—	Red	146–148 dec.	13.20	13.40

[a] Reported m.p. 117.9°, N. Effremov and A. Tikhomirova, *J. Russ. Phys. Ch. Soc.*, **59**, 337 (1927). [b] Reported m.p. 107.2°, N. Effremov and A. Tikhomirova, J. Russ. Phys. Ch. Soc., **59**, 337 (1927). [c] Reported m.p. 106°, E. Nolting and A. Collin, *Ber.*, **17**, 270 (1884). [d] Reported m.p. 113.1°, N. Effremov and A. Tikhomirova, J. Russ. Phys. Ch Soc., **59**, 337 (1927). [e] Reported m.p. 163°, C. Shinomiya, *Bull. Ch. Soc. Jap.*, **15**, 259 (1940).

Spectroscopic studies. Studies of the ultraviolet and visible spectra of these amine picrates were performed in ethanol solution since the compounds were not sufficiently soluble in a less polar solvent. The spectra obtained were essentially the sum of the absorptions due to the two components, which indicates almost complete dissociation at such low concentrations.

Infrared studies were more rewarding, and several bands characteristic of amine salts and picrates were verified. Band I, which falls within the range of 1637–1605 cm.$^{-1}$ for the methyl- and ethylpicrates and between 1616 and 1590 cm.$^{-1}$ for the dimethylpicrates is the aromatic C=C in-plane vibration.[6,7]

Band II, which with three exceptions, falls within the narrow limits of 1582–1567 cm.$^{-1}$ is C=C stretching in a conjugated aromatic ring.[8]

Band III, one of the strongest and more irregularly shaped bands is C—NO_2 asymmetric stretching vibration, having an average value of 1521 cm.$^{-1}$[9] as compared to 1518 cm.$^{-1}$ as reported by Randle and Whiffen,[10] and 1523 cm.$^{-1}$ as reported by Kross and Fassel.[11]

Band IV is a rather ragged band probably made up of several components including, on the higher wave number side, the symmetrical C—NO_2 stretching vibration. The range varied from 1346 cm.$^{-1}$ to 1300 cm.$^{-1}$ with two peaks generally at 1330 cm.$^{-1}$ and 1310 cm.$^{-1}$

Band V, which appears in the range of 1279 cm.$^{-1}$ to 1253 cm.$^{-1}$, appears in all the picrates except those of carbazole. None of the free amines nor free picric acids exhibit this peak; however, the sodium salts of the picric acids do show this absorption, and, therefore, it appears to be a picrate salt (C—O$^-$) stretching vibration.

Band VI is believed to be an aromatic absorption. Unfortunately, little work has been done on the vibrations of penta- and hexa-substituted benzenes which appear in this region. The range of values is 1183 cm.$^{-1}$ to 1151 cm.$^{-1}$ The values for the dimethylpicrates average about 12 cm.$^{-1}$ higher than for the methyl- and ethylpicrates.

There are bands which are characteristic of the picrates of primary amines. The main band at approximately 3200 cm.$^{-1}$ is a NH_3^+ stretching frequency,[12] and our values ranged from 3310 to 3150 cm.$^{-1}$

The weaker band at about 2600 cm.$^{-1}$ is thought to be a NH_3^+ vibration, but it is too weak to be of much use in identification processes. Our values ranged from 2645 to 2565 cm.$^{-1}$ Butylamine hydrochloride[13] is reported to absorb at 2625 cm.$^{-1}$ to 2590 cm.$^{-1}$

There is a band that is characteristic of picrates of secondary amines. This band is comparatively strong among secondary amine vibrations, and is thought to be a NH_2^+ stretching vibration, and is in the large range of 2800 cm.$^{-1}$ to 2000 cm.$^{-1}$[14] Our values ranged from 2570 to 2420 cm.$^{-1}$

There are bands which are characteristic of tertiary amine picrates. The band around 2600 cm.$^{-1}$ is a NH^+ stretching frequency.[15] This band is very weak and thus is not too reliable. Our values ranged from 2670 to 2500 cm.$^{-1}$ The other band around 2100 cm.$^{-1}$, which appears in amines having nitrogen in a pyridine structure is due to C = NH^+.[16] Our values ranged from 2165 to 2030 cm.$^{-1}$

The infrared spectra of the picrates of carbazole are of special interest. The sharp NH stretching band at 3430 cm.$^{-1}$ in the free amine remains unchanged in the picrates. The band found in all the other compounds at 1265 cm.$^{-1}$ and attributed to C—O$^-$ stretching is not present in these compounds. There are no bands in the 2700–2300 cm.$^{-1}$ region where NH_2^+ would be expected to absorb. Finally, the aromatic bands of carbazole at 750 and 725 cm.$^{-1}$ are slightly shifted to higher wave numbers. The evidence leads to the belief that the carbazole picrates are true complexes and not salts.

EXPERIMENTAL

Microanalyses by Microtech laboratories in Skokie, Ill.

All infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using nujol mulls. The ultraviolet and visible spectra were recorded on a Beckman DK-2 spectrophotometer using concentrations of approximately 5 $\times 10^{-6}$ moles per liter.

Preparation of hydrocarbon picrates. The complexes were prepared by heating 1:1 mixtures of the hydrocarbon and the picric acid to be used in a suitable solvent, filtering the solution through a sintered glass filter, and permitting the complex to precipitate.

Melting point diagrams. Mixtures of varying composition were weighed out on an analytical balance into tubes of 8-mm. Pyrex glass previously closed at one end and blown into a small bulb, and the contents melted by dipping into a beaker of Nujol at a temperature several degrees above the melting point of the higher melting component. After cooling, the tubes were broken near the bulb end and the material withdrawn and ground to a fine powder. Capillary tubes were filled and sealed and the melting points determined using a Fisher-Hershberg melting point determination apparatus. Two temperatures were recorded in each case—that at which the first melting of the solid was observed and that at which the entire amount of the solid was completely melted. The melting points of at least two samples of each mixture were recorded so that the points graphed are the results of duplicate runs with agreement to within 1°.

Preparation of amine picrates. Equimolar portions of the two components were allowed to react in a suitable solvent. In most cases alcohols proved acceptable as solvents and this was especially true in the case of the derivatives of pyridine,

(6) H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, *The Infrared Determination of Organic Structures*, Van Nostrand (1949).

(7) N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

(8) Exceptions are: aniline dimethylpicrate (1558 cm.$^{-1}$), *N*,*N*-Dimethylaniline dimethylpicrate (1558 cm.$^{-1}$), and pyridine methylpicrate (1585 cm.$^{-1}$).

(9) Highest value 1543 cm.$^{-1}$ and lowest value 1490 cm.$^{-1}$

(10) R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952).

(11) R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, **78**, 4225 (1956).

(12) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955) and 2712 (1956).

(13) J. Despas, J. Khaladji, and R. Vergoz, *Bull. Soc. Chim. Fr.*, 1105 (1953).

(14) R. A. Heacock and L. Marion, *Can. J. Chem.*, **34**, 1782 (1956).

(15) J. Bellanato and J. Barcelo-Matutano, *Anales. real. Soc. Espan. fis. y quim.*, **52B**, 469 (1956).

(16) B. Witkop, *Experientia*, **10**, 420 (1954).

2-picoline, 2,6-lutidine, quinoline, and morpholine, since the picrates of these amines have quite low solubility in alcohol. On the contrary, the formation of the picrates of aliphatic amines in alcohol was not too successful, as the picrates have about the same or even more solubility in alcohol than the picric acids themselves. Ethyl ether was found to be a satisfactory solvent for the precipitation of picrates of aliphatic amines and picrates of 1-naphthylamine. The picrates of aniline were easily prepared from boiling water. The melting points of the picrates were determined in an evacuated capillary tube using a copper melting point block. Values obtained in an open melting point heated block were as much as 40° lower. To obtain reasonable duplication, the melting points were recorded using a temperature gradient of 1°/min.

CHICAGO 26, ILL.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF PUERTO RICO AT MAYAGUEZ AND DALHOUSIE UNIVERSITY]

Saponification of Methyl-Substituted α-Butyrolactones

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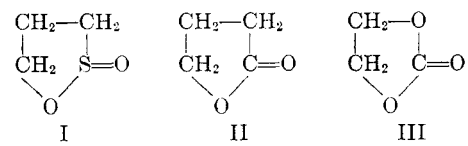
Received December 8, 1960

The rates of saponification of γ-butyrolactone and monomethyl and *gem*-dimethyl γ-butyrolactones have been measured in 92.3% ethanol at 0° and 25°. The observed differences in rate cover a range of only about 4-fold, much less than anticipated from data on esters, and suggest that the steric effect of the methyl groups is relatively unimportant in the hydrolysis of these lactones.

The effect of alkyl groups on the ease of ring opening of carbon rings is still not fully understood,[2] and little experimental work has been published on this, although Bordwell and co-workers[3] have recently reported a study of the unimolecular solvolysis of sultones (I) (cyclic sulfonates). Many ring-opening reactions, however, proceed by bimolecular hydrolysis and this paper reports a study of the effect of methyl groups on the rates of saponification of γ-butyrolactone (II) (see Table I).

The basic hydrolysis of γ-butyrolactones is very rapid in aqueous solution[4] and was accordingly studied in 92% ethanol, in which solvent the rate



I II III

can be conveniently followed by titration (see experimental), which also served as a check on the purity of the lactones used. The mechanism of basic hydrolysis of γ-butyrolactone has been well established as involving an initial nucleophilic attack of hydroxyl (or ethoxyl) ion on the carbonyl carbon atom, followed by acyl-oxygen fission.[5] No uncatalyzed solvolysis has been detected.[6] The observed rates of saponification (Table I) covered a range of some 4-fold, all the methylated γ-butyrolactones hydrolyzing at 25° at a lower rate than γ-butyrolactone itself, in the order H $<$ α CH_3 $<$ γ CH_3 $\sim$ β CH_3 $<<$ γ,γ$(CH_3)_2$ $<$ ββ $(CH_3)_2$ $<<$ αα $(CH_3)_2$. The differences are considerably less than those which might be expected from the rates of saponification of esters. Thus the relative rates for ethyl propionate, isovalerate and pivalate (analogous in substitution of γ-butyrolactone and β-methyl and α,α-dimethyl-γ-butyrolactone) are 100:12:1.3 (in 85% ethanol at 25°).[7] Similar small differences have been noted in the saponification of γ-butyrolactone and γ-methyl and γ,γ-dimethyl-γ-butyrolactone in 43% acetone at 20° (ratio 100:39:12.6),[8] for γ-butyrolactone and α-methyl, γ-methyl, and γ,γ-dimethyl-γ-butyrolactone at 25° (ratio 100:69:50:18),[9] and in the acid-catalyzed hydrolysis.[9,10] The energies of activation for the saponification of the butyrolactones are more constant[8] than for ester hydrolysis, although the log PZ factors are more variable (ethyl propionate and pivalate have Eact. 14.7 and 17.1 kcal and log PZ 8.0 and 8.2, respectively[7c]).

The ring of γ-butyrolactone is probably nearly planar, although eclipsed non-bonded interactions between the hydrogen atoms on the β- and γ-

(1)(a) University of Puerto Rico at Mayaguez, P. R.; (b) Dalhousie University, Halifax, N. S., Canada. Taken from M.Sc. Thesis, September, 1959.

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(8) C. M. Stevens and D. S. Tarbell, *J. Org. Chem.*, **19**, 1996 (1954).

(9) H. Sebelius, Inaugural dissertation, Lund, 1927, reported by W. Hückel, *Theoretical Principles of Organic Chemistry*, Elsevier, New York, 1958, p. 892. The solvent is not given (presumably water) and the original reference was not available to us.

(10) O. H. Wheeler and E. E. Granell, unpublished results.