agent, the resulting mixture was stirred for several minutes longer, heated under reflux for two hours and then allowed to cool and stand overnight at room temperature. The reaction flask was cooled in an ice–water-bath and the pale yellow product decomposed with dilute hydrochloric acid. A 300-ml. quantity of diethyl ether was added to dilute the benzene solution of 2-(2′-methoxybenzoyl)-benzoic acid and 2,2-di-*o*-anisylphthalide. The ether–benzene layer was extracted with potassium carbonate solution, and the carbonate extract then run dropwise into vigorously stirred, ice-cold hydrochloric acid. In this way the keto acid first separated as a pasty mass which soon became solid. This pale fawn-colored, granular solid was filtered off and washed with cold diethyl ether. Upon drying, 34.5 g. (54%) of crude acid was obtained. After four recrystallizations from glacial acetic acid, 2-(2′-methoxybenzoyl)-benzoic acid was secured in the form of short, colorless, small prisms; m. p. 143–143.5°; yield 30 g. (47%, based on phthalic anhydride). Sieglitz[2] reported 144–145° as the m. p. of this acid.

Anal. Neutralization equivalent, calcd. for $C_{15}H_{12}O_4$: 256.2. Found: 257.9.

From the above-mentioned benzene–ether layer, after the potassium carbonate extraction and concentration of the solution to a small volume, a colorless powder was obtained. This material, 2,2-di-*o*-anisylphthalide, when recrystallized three times from glacial acetic acid, formed small, colorless crystals, m. p. 148–149°; yield 10.5 g. (18%, based on *o*-bromoanisole). The phthalide was found to be soluble in concentrated sulfuric acid with a very deep violet color which gradually changed to ruby-red and finally to orange.

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The Dissociation of Hexaarylethanes. XIV.[1] Ethanes Derived from Mixtures of Triaryl Halides

BY C. S. MARVEL AND CHESTER M. HIMEL

Since symmetry seemed to be important in connection with the influence of substituents on the degree of dissociation of triarylmethyls, it occurred to us that treating an equimolecular mixture of two triarylmethyl halides with silver might produce a truly unsymmetrical ethane rather than a mixture of ethanes. Table I contains a list of some mixtures of chlorides which were thus treated and the degree of dissociation calculated from magnetic susceptibility measurements on the assumption that a mixed ethane was formed. In one case (the first in the table) the mixed ethane was prepared by mixing preformed solutions of the individual ethanes rather than by action of silver on the mixed halides.

TABLE I

DISSOCIATION OF SOME MIXED HEXAARYLETHANES

Chlorides used	$-\chi \times 10^6$	α at 0.1 *M*, %	α of corresponding ethane at 0.1 *M*, %	Ref.
o-Chlorophenyldiphenylmethyl	0.6620	14 ± 2	12 ± 1	1
o-Bromophenyldiphenylmethyl			17 ± 1	1
o-Tolyldiphenylmethyl	.6320	26 ± 2	25 ± 1	2
α-Naphthyldiphenylmethyl			27 ± 2	3
o-Tolyldiphenylmethyl	.6282	27 ± 2	25 ± 1	2
Di-*o*-tolylphenylmethyl			82 ± 2	4
Tri-*p*-diphenylmethyl	.6765	25 ± 3[a]	25 ± 5	3
Tri-β-naphthylmethyl			25 ± 5	3
p-*t*-Amylphenyldiphenylmethyl	.6985	3.5 ± 1	8.0 ± 1	4
Phenyl-di-*p*-*t*-amylphenylmethyl			9.0 ± 1	4
Tri-*p*-*t*-butylphenylmethyl	.6997	3.5 ± 1	20 ± 4	4
p-*t*-Butylphenyldiphenylmethyl			7.5 ± 1	4

[a] The actual measurement was made at 0.025 *M* and the dissociation at this concentration was 43 ± 4%. The value in the table was calculated by means of the mass law.

The method and apparatus have been described in previous papers in this series. It can be seen readily that the observed degrees of dissociation are not the average of the two simple ethanes, but in general are lower than this value. There are several equilibria possible in this complicated system and a complete appraisal of the significance of these experimental results will not be possible until these equilibria are more thoroughly studied. Since it seems unlikely that this can be done soon, these results are recorded.

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(1) For the thirteenth communication see *J. Org. Chem.*, **7**, July (1942).

(2) Marvel, Mueller, Himel and Kaplan, THIS JOURNAL, **61**, 2771 (1939).

(3) Marvel, Shackleton, Himel and Whitson, *ibid.*, **64**, 1824 (1942).

(4) Marvel, Kaplan and Himel, *ibid.*, **63**, 1892 (1941).

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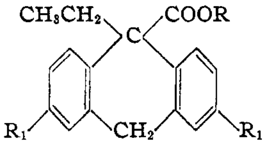
The Reaction of Furoic Acid with Aromatic Compounds. III

BY CHARLES C. PRICE, E. C. CHAPIN AND MARTIN RIEGER

The isolation of methyl 9-ethyl-9,10-dihydro-9-anthroate (I) from the aluminum chloride catalyzed reaction of methyl furoate with benzene[1] suggests the presence of the corresponding acid (II) in the mixture obtained from a similar re-



I ($R = CH_3, R_1 = H$)
II ($R = R_1 = H$)
III ($R = H, R_1 = CH_3$)

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(1) Price and Huber, THIS JOURNAL, **64**, 2136 (1942).

action with furoic acid.[2] Oxidation of the crude mixture from the latter reaction to yield anthraquinone has already been presented as evidence for the formation of an acid with an anthracene nucleus.[2] This observation has now been substantiated by degradation of the crude reaction mixture to anthracene by subjecting it to soda-lime distillation. Crystallization from benzene of the oily distillate so obtained yielded anthracene in 10% yield, m. p. 208–210°. Its identity was checked by a mixed melting point determination.

Thus, although the pure acid has yet to be isolated, analogy with the methyl furoate reaction supports the suggestion that the anthroic acid present in the mixture of acids formed from benzene and furoic acid is 9-ethyl-9,10-dihydro-9 anthroic acid (II).

The oily residue left after crystallization of anthracene from the soda-lime distillate was dehydrogenated with sulfur to yield 1,4-diphenylnaphthalene, previously obtained as a degradation product of the acid mixture. It is believed to be derived from 1,4-diphenyl-1,2,3,4-tetrahydro-1-naphthoic acid.[2]

Soda-lime distillation of the crude acid mixture obtained by reaction of toluene and furoic acid yielded 2,7-dimethylanthracene, m. p. 238–239°, which showed no depression in melting point when mixed with an authentic sample. Isolation of this hydrocarbon indicates that this reaction also gives rise to an anthroic acid. Again, the pure acid has yet to be isolated, but analogy with the product from benzene, as well as consideration of the simplest product of the reaction, 6-methyl-1-naphthoic acid, suggests that the anthracenic component of the toluene-furoic acid reaction may be 3,6-dimethyl-9-ethyl-9,10-dihydro-9-anthroic acid (III).

Repeated efforts to isolate a substance from the crude toluene product, corresponding to the 1,4-diphenylnaphthalene obtained from the benzene product, have failed. Attempted decarboxylation of the toluene product by heating with copper chromite in quinoline, successful for the benzene product, yielded a black, intractable tar from the toluene product. Evidently the tar was formed by oxidation, since the black powdery copper chromite catalyst was transformed to a mixture of green chromium oxide powder and small bright balls of metallic copper. Treatment with sulfur or selenium of the pale yellow oil from the mother liquor of the soda-lime distillate led to copious evolution of hydrogen sulfide or selenide, but no crystalline product could be isolated.

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[2] Price, Chapin, Goldman, Krebs and Shafer, THIS JOURNAL, **63**, 1857 (1941).

A Color Test for Citrinin and a Method for its Preparation

BY HENRY TAUBER, STEPHEN LAUFER AND MILTON GOLL

The following is a color test for citrinin and a method for the preparation of the anti-bacterial substance.

The Color Test.—One mg. of citrinin (prepared as given below) is dissolved in 0.5 cc. of 95% alcohol and 0.3 cc. of 3% hydrogen peroxide is added. The mixture is agitated for one minute. The intense yellow solution becomes first colorless, then light brown. Hereafter, 0.3 cc. of 0.2 *N* sodium hydroxide is added. A deep wine-red color forms at once. On the addition of 0.3 cc. of 0.2 *N* sulfuric acid the wine-red color turns orange-yellow and on the addition of a further 0.3 cc. of 0.2 *N* sodium hydroxide the wine-red color reappears again. In a control tube in which water is substituted for hydrogen peroxide an orange-yellow color develops. This color reaction with sodium hydroxide from intense yellow to orange-yellow was also noted by A. C. Hetherington and H. Raistrick [*Trans. Roy. Soc.*, London, **B220**, 279 (1931)] who stated that "Citrinin is readily soluble in aqueous NaOH giving rise to an orange-yellow solution which on standing changes color to orange-red." This is indeed the case when a fairly concentrated sodium hydroxide solution is added to a citrinin solution. We found, however, that when 0.25 to 0.5 cc. of 0.02 *N* sodium hydroxide is added to 1 mg. of citrinin in 0.5 cc. of ethyl alcohol, a very light pink color forms which does not change in intensity on further addition of the alkali or on standing. H. W. Hirschy and Ruoff [THIS JOURNAL, **64**, 1490 (1942)] have recently observed that above *p*H 9.9 the color of a citrinin solution changed from orange-pink to cherry-red.

Continued exposure of citrinin to dioxane results in a hydrogen peroxide-like reaction. On long exposure to air alcoholic citrinin solutions undergo certain changes which do not appear to be identical with hydrogen peroxide-oxidation.

The hydrogen peroxide–sodium hydroxide color reaction is also given by the original cultures, by the acid precipitated crude citrinin, and after it had been recrystallized from 95% alcohol. Citrinin solutions that have been treated with sodium hydroxide and readjusted to the original *p*H do not give the hydrogen peroxide–sodium hydroxide reaction.

Penicillin obtained from *P. notatum* (A. T. C. C.) gives a lemon-yellow color with this test.

Preparation of Citrinin.—1500 cc. of the filtrate of a fourteen-day old culture of *P. citrinum* prepared according to H. Raistrick and G. Smith [*Chemistry and Industry*, **60**, 828 (1941)] is adjusted to *p*H 3.0 to 2.5 with *N* hydro-