aniline, *less* than the theoretical amount of nitrogen was evolved on heating.

Furthermore, when slightly more than one equivalent of morpholine was added to a solution of benzazide in aniline, no gas at all was evolved on heating. If the added amount of morpholine was insufficient to react with benzazide according to equations E and F, then some nitrogen was evolved.

Salt Effect.—Investigation of the salt effect in this reaction yielded the data appearing in Table III.

The slight changes in rate with increasing salt concentration are within the limits of accuracy of the rate constant determinations.

TABLE III

SALT EFFECT AT 65°

Run no.	Salt	Solvent	Molarity of Salt	Molarity of Azide	Rate per hr.
55	2,4-Dinitrophenyl-	*n*-Propanol	0.0226	0.1202	0.330
56	Pyridinium chloride	*n*-Propanol	.0123	.1359	.323

The average rate in the *n*-propanol salt solutions, 0.3265/hour, agrees well with the mean rate in *pure* *n*-propanol, 0.328/hour. The lack of a salt effect is in accord with the theoretical conclusion of Wallis[2] about the mechanism of the reaction.

Summary

1. The rate of decomposition of benzazide to phenyl isocyanate and nitrogen alone and in thirteen solvents has been measured at 55, 65 and 75°.

2. No simple correlation between rate constants and dielectric constant, dipole moment, viscosity or boiling point of the solvents is evident.

3. Energies and entropies of activation for the decomposition of benzazide alone and in these solvents have been calculated. Since large energies and entropies of activation are associated with small rate constants in general, solvation of the activated complex is indicated.

4. No surface or salt effect is evident.

5. The decomposition of benzazide in primary and secondary aliphatic amines does not occur since reaction to form substituted benzamides is more rapid.

6. In acetic acid a secondary reaction leading to the formation of carbon dioxide occurs. The kinetics remain unimolecular. In nitromethane, another unidentified gas is obtained and the kinetics are complex.

7. Pure benzazide freezes and melts at 27.2° as determined by time–temperature cooling and heating curves. The present literature value is 32°.

8. The significance of the relatively large entropy change remains obscure.

COLUMBUS, OHIO RECEIVED JUNE 17, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE GEORGIA SCHOOL OF TECHNOLOGY]

The Tolylmercaptopropanones and their Condensation with Isatins

BY O. NEWELL AND PAUL K. CALAWAY

In a previous paper[1] we have reported the utilization of 1-phenylmercapto-2-propanone in the preparation of substituted cinchoninic acids by the method of Pfitzinger.[2] The availability of the thiocresols suggested the preparation of the 1-tolylmercapto-2-propanones and their ultimate condensation with isatin and 5-methylisatin, respectively, to produce six examples of a new type of substituted cinchoninic acid.

In our initial synthesis of 1-(*p*-tolylmercapto)-2-propanone we followed the method used in earlier work[1] for the preparation of 1-phenylmercapto-2-propanone. The sodium salt of *p*-thiocresol was formed in boiling benzene, and chloroacetone was dropped into the mixture producing 1-(*p*-tolylmercapto)-2-propanone. The latter was purified by distillation under diminished pressure. The yield obtained (55%) was not too good, and the reaction required several hours. Some discoloration of the sodium salt was noticed before the completion of the reaction. Upon repetition of the synthesis, substituting toluene for benzene, and elevating the temperature of reaction to 100°, discoloration of the sodium salt was avoided, the reaction time was appreciably shortened, and the yield of 1-(*p*-tolymercapto)-2-propanone was increased to 85%. This percentage yield compares favorably with those reported by Hurd and Perletz[3] in their work on the synthesis of aryloxy ketones.

Experimental

Preparation of 1-(*p*-Tolylmercapto)-2-propanone.—A mixture of 24.8 g. (0.2 mole) of *p*-thiocresol and 200 cc. of toluene was introduced into a 500-cc., three-necked, roundbottomed flask equipped with an efficient, mercury-sealed mechanical stirrer, a dropping funnel and a condenser. The stirrer was started and 4.6 g. (0.2 mole) of finely divided sodium was added over a period of thirty minutes. After heating for two hours on a boiling water-bath all the sodium had dissolved and the sodium salt of the *p*-thiocresol separated as a white solid. The reaction mixture was allowed to cool to room temperature, 18.5 g. (0.2 mole) of chloroacetone was dropped in over a period of ten

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[1] Knight, Porter and Calaway, THIS JOURNAL, **66**, 1893 (1944).

[2] (a) Pfitzinger, *J. prakt. Chem.*, **33**, 100 (1886); (b) **38**, 582 (1888); (c) **56**, 283 (1897).

[3] Hurd and Perletz, THIS JOURNAL, **68**, 38 (1946).

minutes, and the mixture again heated to complete the reaction. Sodium chloride was removed by filtration and toluene by distillation under diminished pressure. The residual liquid was subjected to distillation and 30.6 g. (85% yield) of 1-(*p*-tolylmercapto)-2-propanone was obtained as a pale yellow liquid boiling over the range 133–135° (7–9 mm.).

Preparation of 1-(*m*-Tolylmercapto)-2-propanone.—This compound was prepared by the method outlined for the *p*-isomer, but was obtained in slightly lower yield (78%) as a pale yellow liquid boiling at 142° (8 mm.).

Preparation of 1-(*o*-Tolylmercapto)-2-propanone.—By use of the same general procedure 1-(*o*-tolylmercapto)-2-propanone was obtained in 84% yield as a pale yellow liquid boiling at 138° (8 mm.).

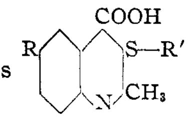
Preparation of 5-Methylisatin.[4]—This compound was prepared by the procedure outlined in "Organic Syntheses," and the product was purified by recrystallization from glacial acetic acid.

Preparation of 3-(*p*-Tolylmercapto)-4-quinaldinecarboxylic Acid.—Seventeen and one-tenth grams (0.116 mole) of isatin was dissolved in 200 cc. of thirty-three per cent. aqueous potassium hydroxide solution, and 20.95 g. (0.116 mole) of 1-(*p*-tolylmercapto)-2-propanone was added. The resulting mixture was heated under reflux on the steam-bath for eight hours, boiled with Norite and filtered. The clarified solution was poured over an equal volume of ice and made definitely acidic by the addition of acetic acid. The cream colored solid was dissolved in potassium hydroxide solution and again treated with activated charcoal. The solution was cooled in ice and made barely acidic by the addition of acetic acid. The 3-(*p*-tolylmercapto)-4-quinaldinecarboxylic acid separated as a light cream-colored precipitate (75% yield). Dried over anhydrous calcium chloride, the product retained two molecules of water of hydration (as indicated by the analytical data for nitrogen content) which were removed by drying in a vacuum desiccator over phosphorus pentoxide. The product melted with decomposition at 274°.

The remaining 3-tolylmercaptocinchoninic acids were formed in essential accordance with this general procedure. Table I contains the data on these preparations.

TABLE I

3-TOLYLMERCAPTOCINCHONINIC ACIDS



R—	R′—	Yield, %	M. p., °C. (cor.)	N anal., % found[a]	Neut. equiv. found[b]
H	*p*-Tolyl	75	274	4.52	316
H	*m*-Tolyl	90	258	4.48	313
H	*o*-Tolyl	60	278	4.41	311
CH_3	*p*-Tolyl	90	275	4.27	323
CH_3	*m*-Tolyl	70	260	4.30	326
CH_3	*o*-Tolyl	66	266	4.34	328

[a] Calcd.: N, 4.53 for R = H; N, 4.33 for R = CH_3.

[b] Calcd.: neut. equiv., 309 for R = H; neut. equiv., 323 for R = CH_3.

Summary

1. Pfitzinger's method has been extended to include the utilization of the tolylmercaptopropanones in the synthesis of six substituted quinoline acids from isatin and 5-methylisatin, respectively.

ATLANTA, GEORGIA RECEIVED SEPTEMBER 3, 1946

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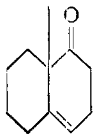
[4] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 321.

[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

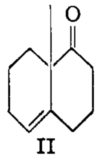
The Synthesis of Condensed Ring Compounds. XV.[1] A New 9-Methyloctalone[2]

BY ADAM M. GADDIS AND LEWIS W. BUTZ

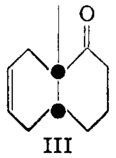
Two 9-methyloctalones have previously been prepared and partly characterized, the position of the carbon–carbon double bond being still unknown.[3] The probable structures are 10-methyl-4-naphthiten-1-one (I) and 10-methyl-5-naphthiten-1-one (II). We now report on a third 9-methyloctalone which was first prepared by Nudenberg.[4] The position of the carbon–carbon double bond in this ketone also remains undetermined. The compound is probably *cis*-10-methyl-7-naphthiten-1-one (III).



I



II



III

When 1,3-butadiene and an excess of 1-methyl-1-cyclohexen-6-one are held at 200° for about forty hours and the resulting mixture is distilled, about 80% of the methylcyclohexenone is recovered unchanged and a higher boiling ketone is obtained in about 30% yield calculated on the methylcyclohexenone consumed. This product has the composition and properties of compound III or an isomer with the C═C bond in another position. It appears to consist, at least chiefly of one isomer for several derivatives were prepared in high yield and adsorption and elution of the 2,4-dinitrophenylhydrazone, employing a column of alumina, indicated a single substance.

Controlled catalytic hydrogenation gave a known 9-methyldecalone, probably the *cis* isomer.[5] The identity was established by the constants of the dihydroketone and its derivatives and by direct comparison of the 2-benzal-9-methyl-1-decalone by melting point of the mixture

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(1) For the preceding paper see *J. Org. Chem.*, **8**, 509 (1943).

(2) This work was supported by an allotment from the Special Research Fund (Bankhead–Jones Act of June 29, 1935). Not copyrighted.

(3) Plentl and Bogert, *J. Org. Chem.*, **6**, 669 (1941).

(4) Nudenberg and Butz, THIS JOURNAL, **65**, 1436 (1943).

(5) Johnson, *ibid.*, **65**, 1317 (1943).