made. Increasing the final $p$H to 8.3 in the buffered solvent system resulted in the slow hydrolysis of 1,2-naphthoquinone-1-benzimide (rate constant: $0.67 \times 10^{-4}$ sec.$^{-1}$ at 25°). The rate of hydrolysis of 1,2-naphthoquinone-1-acetimide in the buffered aqueous dioxane at $p$H 8.3 was almost three times faster (rate constant: $1.80 \times 10^{-4}$ sec.$^{-1}$ at 25°) than the rate of hydrolysis of 1,2-naphthoquinone-1-benzimide in the same solvent system. After a solution of 1,2-naphthoquinone-1-acetimide in buffered aqueous dioxane at $p$H 8.3 had stood for several hours, the visible spectrum of the solution was identical with that of a solution of 1,2-naphthoquinone.

## EXPERIMENTAL

1,2-Naphthoquinone,[5] 1,2-naphthoquinone-1-imine,[3] 1,2-naphthoquinone-1-acetimide[4] and 1,2-naphthoquinone-1-benzimide[6] were prepared by published methods. Dioxane was purified according to Fieser.[7] The visible and ultraviolet spectra were recorded on a Beckman Model DR Spectrophotometer.

*1,2-Naphthoquinone-1-imine in aqueous ethanol.* A comparison of the ultraviolet absorption spectra of 1,2-naphthoquinone and 1,2-naphthoquinone-1-imine is shown in Fig. 1. The rate of decrease in absorbance at 259 mμ was used to measure the rate of hydrolysis of 1,2-naphthoquinone-1-imine in aqueous ethanolic solutions. The concentration of 1,2-naphthoquinone-1-imine was calculated from the equation:

$$[\mathrm{QI}]_t = \frac{\mathrm{E}_t - [\mathrm{QI}]_0 \cdot \epsilon_{\mathrm{Q}}}{\epsilon_{\mathrm{QI}} - \epsilon_{\mathrm{Q}}}$$

where

$[\mathrm{QI}]_t$ = concentration (mol. per l.) of 1,2-naphthoquinone-1-imine at time, $t$
$\mathrm{E}_t$ = absorbance at time, $t$
$[\mathrm{QI}]_0$ = initial concentration (mol. per l.) of 1,2-naphthoquinone-1-imine
$\epsilon_{\mathrm{QI}}$ = molar extinction coefficient of 1,2-naphthoquinone-1-imine at 259 mμ ($\log \epsilon = 4.30$)
$\epsilon_{\mathrm{Q}}$ = molar extinction coefficient of 1,2-naphthoquinone at 259 mμ (log • = 4.17).

The first order rate constants were calculated from the data obtained from the plot of the log of the concentration of 1,2-naphthoquinone-1-imine versus time in minutes. The rate plots were linear for the time intervals observed: 60 min. for 95–40% ethanol, 30 min. for 25% ethanol and 10 min. for 10% ethanol.

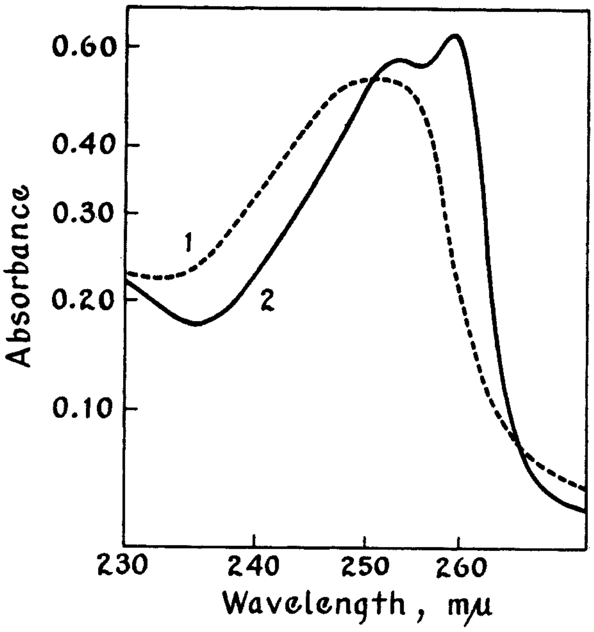

Fig. 1. Ultraviolet absorption spectra of 1,2-naphthoquinone (1) and 1,2-naphthoquinone-1-imine (2) in 95% ethanol

*1,2-Naphthoquinone-1-acetimide and 1,2-naphthoquinone-1-benzimide in aqueous dioxane.* 1,2-Naphthoquinone-1-acetimide and 1,2-naphthoquinone-1-benzimide have absorption maxima at 360 mμ in aqueous dioxane (20% dioxane by volume). The position of the maxima did not shift as the $p$H of the solution was changed from 6.1 to 8.3. The concentrations of solutions of 1,2-naphthoquinone-1-acetimide ($\log \epsilon_{360} = 3.58$) and of 1,2-naphthoquinone-1-benzimide ($\log \epsilon_{360} = 3.68$) were determined from their absorbancies at 360 mμ. Since the rate of hydrolysis of these quinone imides was only slight, absorption at 360 mμ due to the hydrolysis product, 1,2-naphthoquinone, was negligible during the initial time periods.[8]

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(5) L. F. Fieser, *Org. Syntheses*, **Coll. Vol. II**, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 430.

(6) R. Adams and J. M. Stewart, *J. Am. Chem. Soc.*, **74**, 5876 (1952).

(7) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd Ed., D. C. Heath and Company, New York, N. Y., 1955, p. 285, procedure (a).

(8) Present address: Radioisotope Service, VA Medical Teaching Hospital, Memphis 15, Tennessee.

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# 2-Imino-4-oxo-5-thiazolidineacetic Acid and Its Derivatives

A. N. Arakelian, H. Dunn, Jr., L. L. Grieshammer, and L. E. Coleman

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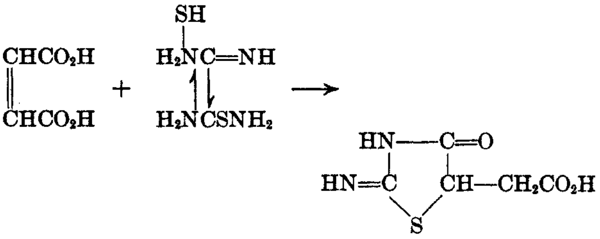
Tambach[1] and Andreash[2] in 1894–1895 reported that thiourea reacts in the enol form with maleic acid or fumaric acid to yield the 2-imino-4-oxo-5-thiazolidineacetic acid, I. Structure was proved



I

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(1) R. Tambach, *Lieb. Ann.*, **280**, 233 (1894).

(2) R. Andreash, *Monatsch.*, **16**, 789 (1895).

TABLE I

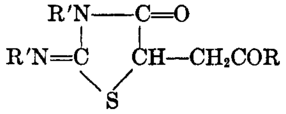
2-IMINO-4-OXO-5-THIAZOLIDINEACETIC ACID AND DERIVATIVES

| Item | Reactant | Solvent | Yield, % | M.P. | Nitrogen, % Calcd. | Nitrogen, % Found | Sulfur, % Calcd. | Sulfur, % Found |
|---|---|---|---|---|---|---|---|---|
| 1 | Maleic acid | Alcohol | 22 | 246 dec.[a] | 16.05 | 16.00 | 18.43 | 18.32 |
| 2 | Fumaric acid | Alcohol | 74 | 244 dec. | 16.05 | 15.80 | 18.43 | 18.25 |
| 3 | Maleic anhydride | Methyl ethyl ketone | 94 | 246 dec. | 16.05 | 16.10 | 18.43 | 18.39 |
| 4 | Diethyl maleate | Alcohol | 51 | 159–160.5[b] | 13.80 | 14.00 | 15.80 | 16.20 |
| 5 | *N*-Butylmaleimide | Alcohol | 66 | 184–185 | 18.30 | 18.30 | 13.90 | 14.20 |
| 6 | *N*-Octylmaleimide | Alcohol | 73 | 193–195 | 14.20 | 14.70 | 11.20 | 11.20 |
| 7 | *N*-Decylmaleimide | Alcohol | 72 | 197–198.5 | 13.58 | 13.30 | 10.35 | 9.87 |
| 8 | *N*-Dodecylmaleimide | Alcohol | 84 | 197 | 11.80 | 12.20 | 8.98 | 9.08 |
| | | | 1,3-Dibutylthiourea | | | | | |
| 9 | Maleic anhydride | Methyl ethyl ketone | 66 | 82–83 | 9.79 | 9.82 | 11.18 | 11.20 |

[a] 210° dec., ref. 1. [b] 164–166°, ref. 3.

TABLE II

Ultraviolet Absorption Spectra of

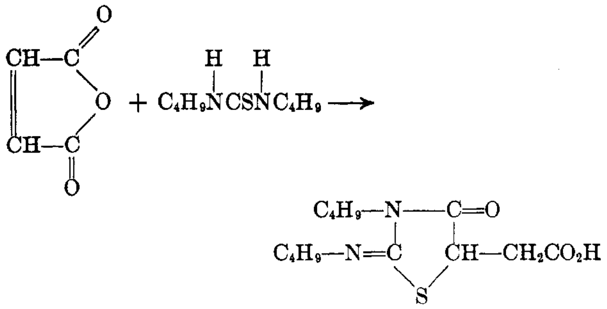


| Item | R | R′ | $\lambda_{max}$, Å | $e \times 10^{-3}$ | $\lambda'_{max}$, Å | $e' \times 10^{-3}$ |
|---|---|---|---|---|---|---|
| 1 | —OH | —H | 2213 | 21.9 | 2503 | 9.6 |
| 2 | —OH | —H | 2217 | 21.2 | 2507 | 9.4 |
| 3 | —OH | —H | 2218 | 20.9 | 2510 | 8.9 |
| 4 | $—OC_2H_5$ | —H | 2218 | 20.5 | 2500 | 9.7 |
| 5 | $—NHC_4H_9$ | —H | 2215 | 23.4 | 2504 | 9.9 |
| 6 | $—NHC_8H_{17}$ | —H | 2216 | 20.5 | 2511 | 8.7 |
| 7 | $—NHC_{10}H_{21}$ | —H | 2218 | 21.2 | 2508 | 9.2 |
| 8 | $—NHC_{12}H_{25}$ | —H | 2211 | 22.2 | 2503 | 9.7 |
| 9 | —OH | $—C_4H_9$ | 2200 | 16.6 | — | — |

by ring degradation. Recently, Japanese workers[3] reported that diethyl maleate reacts with thiourea to give the ethyl ester of I. Benzoyl peroxide was used as catalyst and a low yield of product was obtained. The *N*-ethylacetamide derivative of I was reported by Marrian,[4] who treated *N*-ethyl maleimide with thiourea.

In the course of study in our laboratory, we have made a more complete investigation of the reactions of thiourea with maleic acid, fumaric acid, maleic anhydride, diethyl maleate, and a series of *N*-alkylmaleimides. The resultant compounds were characterized by melting point, chemical analysis, and the infrared and ultraviolet absorption spectra.

Table I describes the various 2-imino-4-oxo-5-thiazolidineacetic acids and derivatives prepared from thiourea. Fumaric acid, maleic acid, diethyl maleate, and the four *N*-alkylmaleimides reacted readily in an alcohol solvent (ethanol-methanol $(8:19)_{wt.}$) to give the desired products. Reaction was slow or incomplete in methyl ethyl ketone. Maleic anhydride, on the other hand, reacted well in methyl ethyl ketone but gave very little reaction in the alcohol solution. Reaction of 1,3-dibutylthiourea with maleic anhydride in methyl ethyl ketone gave the product, II, which is also described in Table I.



II

The ultraviolet absorption data of these compounds are shown in Table II. Compounds prepared from thiourea absorbed at 2211–2218Å and 2500–2511Å while the parent compound from 1,3-dibutylthiourea and maleic anhydride absorbed only at 2200Å. The absence of the 2500Å absorption in II indicates that this peak is probably due to the tautomerism in the cyclic structure, I,

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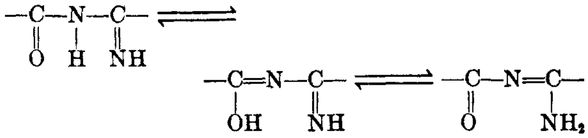
(3) A. Nagasaka, R. Oda, and S. Nukina, *J. Chem. Soc. Japan*, 57, 169 (1954).

(4) D. H. Marrian, *J. Chem. Soc.*, 1797 (1949).



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{NH}{\|}}{C}- \rightleftharpoons -\underset{\underset{OH}{|}}{C}=N-\underset{\underset{NH}{\|}}{C}- \rightleftharpoons -\underset{\underset{O}{\|}}{C}-N=\underset{\underset{NH_2}{|}}{C}-$$

which would be prevented by replacement of the *N*-hydrogen atoms by butyl groups.

### EXPERIMENTAL

The compounds were prepared by heating equimolar amounts of reactants to reflux in either methyl ethyl ketone or the ethanol-methanol solvent for 3–38 hr. Analytical samples were purified by recrystallization from ethanol. All melting points are uncorrected. The ultraviolet absorption spectra were determined in ethanol using a Beckman DK-2 recording spectrophotometer.

*Acknowledgment.* The authors wish to thank Mr. H. Ferber for the chemical analysis of the compounds reported in this paper.

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## Organic Sulfur Compounds. II.[1] Synthesis of Indanyl Aryl Sulfides, Sulfoxides, and Sulfones

ALEXIS A. OSWALD

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Cracked petroleum distillates contain indene and aromatic thiols[2,3] and it is possible that an addition reaction between these compounds can occur. Therefore, a study of these compounds was undertaken with emphasis on the ease with which addition is accomplished and to determine the properties of the resulting indanyl aryl sulfides.

It was found that aromatic thiols readily add to indene even in the absence of any added peroxide catalyst. The addition yielded the same sulfides in the presence or absence of peroxide catalyst. It is assumed, therefore, that thiol-indene addition reactions normally proceed by a radical mechanism. The addition products are formulated as 2-indanyl derivatives, since the ionic addition of acids gives 1-indanyl derivatives.[4,5] The 2-indanyl aryl sulfides obtained are white crystalline compounds soluble in hydrocarbons. An aliphatic thiol, *n*-butanethiol, reacted with indene at a much slower rate than aromatic thiols. The reaction product, 2-indanyl butyl sulfide, is a colorless liquid.

As expected, these sulfides can be oxidized by hydrogen peroxide to the corresponding sulfoxides and sulfones which are less soluble in hydrocarbons in the order mentioned. 2-Indanyl-4-tolyl sulfoxide was also prepared by adding equivalent amounts of 4-toluenethiol and cumene hydroperoxide to an *n*-heptane solution of indene. In this case, the hydroperoxide at first acted as a catalyst for addition, and then as an oxidizing agent for the sulfide formed. Some physical properties and analytical data of the compounds synthesized are shown in Table I.

1-Indanyl aryl sulfides were also synthesized by treating 1-chloroindane[6] with sodium thiophenolates in benzene–isopropyl alcohol. The 1-indanyl, phenyl, and tolyl sulfides prepared were colorless liquids. They had slightly lower boiling points at 2 mm. pressure than the corresponding 2-indanyl aryl sulfides. The main absorption peaks in the spectra of I–II and III–IV, shown in Table I, were the same. However, triplets between 5.2 and 5.6 $\mu$ had peaks at slightly different wave length. To get a more convincing proof of the difference between the 1- and 2-indanyl derivatives, the 1-indanyl sulfides were oxidized to the corresponding sulfones. The latter were white crystalline compounds melting at slightly lower temperatures than their 2-indanyl isomers. Mixed melting-point determinations of the isomers gave a definite depression.

### EXPERIMENTAL

*Materials.* The indene and mercaptans used in the experiments were vacuum distilled under nitrogen before use. The hydrogen peroxide was a Merck reagent (Superoxol) in the form of a 30% aqueous solution. The solvents were C.P. reagents.

*Synthesis of 2-indanyl aryl sulfides.* A 15–100% solution of 0.1 mole of aromatic mercaptan in n-heptane was added to 11.6 g. (0.1 mole) of freshly distilled indene. Although the initial reaction was exothermic, it was necessary, after a few hours, to heat the mixture on a water bath to complete the addition. The products were recrystallized from *n*-heptane or alcohol. The yields and some physical and analytical data are listed in Table I.

The experimental procedure described above was repeated with 4-chlorothiophenol and indene in the presence of 0.76 g. (0.05 mole) of cumene hydroperoxide (added to the indene before the thiophenol). The same sulfide was obtained in a yield similar to the experiment without the hydroperoxide. This latter experiment supports a radical mechanism of the mercaptan addition to indene.[7]

*Synthesis of 2-indanyl aryl sulfoxides.* The 2-indanyl aryl sulfide (0.1 mole) was dissolved in a mixture of 40 ml. acetic anhydride and 20 ml. acetic acid. To the solution, 0.1 mole

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(1) For the preceding communication of this series, see *J. Org. Chem.*, **24**, 443 (1959).

(2) A. N. Sachanen, *The Chemical Constituents of Petroleum*, Reinhold Publishing Corp., New York, N. Y., 1945, p. 265.

(3) G. S. Windle, *Petroleum Refiner*, **23**, No. 2, 83 (1944).

(4) W. J. Pope and J. Read, *J. Chem. Soc.*, **101**, 758 (1912).

(5) R. Weissgerber, *Ber.*, **44**, 1436 (1911).

(6) 1-Chloroindane was synthesized according to Weissgerber[5] by the introduction of hydrogen chloride into cool indene. It was observed that at the low temperature, 1 mole of indene adsorbed about 2 moles of hydrogen chloride while the mixture turned red. (Details in Experimental.)

(7) E. Müller, *Methoden der organischen Chemie* (Houben-Weyl), G. Thieme Verlag, Stuttgart, W. Germany, 1955, Vol. 9, p. 120.