in the cold to furnish 136 mg. (67% yield) of colorless platelets melting at 133.5–134.0°. The mixed melting point with commercial sebacic acid (m.p. 133–134°) was 133–134°.

5,5''-Diacetyl-2,2',5',2''-terthienyl (V).—A solution of 105 mg. of pure IV m.p. 94–95°, and one drop of 85% phosphoric acid in 1.25 ml. of acetic anhydride was heated for one hour at 110°, while protected from moisture. The solution was then poured over 25 g. of crushed ice and the brown-yellow solid (130 mg.) removed by filtration. One recrystallization from dioxane yielded 86 mg. (61%) of red-orange platelets melting at 242–245°. Sublimation at 225–230° (0.3 mm.) furnished 72 mg. (51%) of pure yellow platelets of V, m.p. 249–250°.

Anal. Calcd. for $C_{16}H_{12}O_2S_3$: C, 57.83; H, 3.61. Found: C, 57.84; H, 3.64.

Reductive Desulfurization of V.—When 35 mg. of V was desulfurized in the usual manner 21 mg. (80% yield) of colorless platelets, m.p. 67–68°, was obtained. Oxidation of this (presumed) 2,15-hexadecane diol with 1.5 ml. of glacial acetic acid and 50 mg. of chromium trioxide furnished 18 mg. (69% from V) of hexadecane-2,15-dione, m.p. 83–85°, after one recrystallization from aqueous methanol (reported[6] m.p. 82.5°).

Separation of Monocarboxylic Acids XIII and XIV.—The lithiation and carbonation of 2.10 g. of 2,3'-bithienyl[15] was carried out as described above for 2,2'-bithienyl, using 2.10 g. of bromobenzene and 1.90 g. of lithium in 130 ml. of ether. The crude carbonated mixture was dissolved in 5 *N* sodium hydroxide solution. Insoluble material furnished 0.3 g. (15%) recovered 2,3'-bithienyl. Acidification of the filtrate yielded 1.71 g. (75%) of crude mixture of acids. This dried acid mixture was stirred with heptane–benzene (4:1) and the solid remaining (80 mg.) removed by filtration. This solid, m.p. 270–280°, presumably consisting of dibasic acid(s) was not investigated further. Upon cooling the organic filtrate in ice, 0.62 g. (38%) of crude acid, m.p. 156–168°, crystallized. Several crystallizations from the same solvent mixture furnished pure 2,3'-bithienyl-5'-carboxylic acid (XIV), m.p. 173–175° (for analysis see Table I). The filtrate was concentrated to a small volume to furnish 0.85 g. (52%) of acid XIII, m.p. 94–105°. Three crystallizations from petroleum ether (b.p. 60–80°) furnished pure 2,3'-bithienyl-2'-carboxylic acid, m.p. 107–109° (for analysis see Table I).

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, ORGANIC CHEMICALS DIVISION, AMERICAN CYANAMID CO.]

Novel Reactions of 2-Naphthol with Thioglycolic Acid and Other Mercaptans[1]

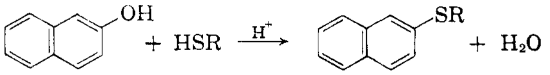
BY F. M. FURMAN, J. H. THELIN, D. W. HEIN AND W. B. HARDY

RECEIVED MAY 29, 1959

Two unusual reactions of 2-naphthol with thioglycolic acid have been found. An alkaline-catalyzed reaction gave 2-hydroxy-1-naphthaleneacetic acid in 89% yield. Acid catalysis gave (2-naphthylthio)-acetic acid in 87% yield. The latter reaction is general for naphthols and other mercaptans, thus providing a useful synthetic route to alkyl and aryl naphthyl sulfides.

Thioglycolic acid (mercaptoacetic acid) has been found to react with 2-naphthol in two novel and divergent ways. With an alkaline catalyst, hydrogen sulfide is evolved and 2-hydroxy-1-naphthaleneacetic acid is formed. But with an acid catalyst, (2-naphthylthio)-acetic acid is obtained. The acid-catalyzed reaction was extended to alkyl and aryl mercaptans and the corresponding 2-naphthyl sulfides were obtained. Thioglycolic acid reacts similarly with 1-naphthol and 1,5-naphthalenediol. Thus, the acid-catalyzed reaction appears to be general with naphthols.

The Acid-catalyzed Reaction.[2]—2-Naphthol was heated at 110–120° with various mercaptans for about 16 hours in the presence of acid catalysts (*e.g.*, *p*-toluenesulfonic acid) without a solvent. 2-Naphthyl sulfides were conveniently obtained in good yields. Examples of this reaction, together with the yields, are

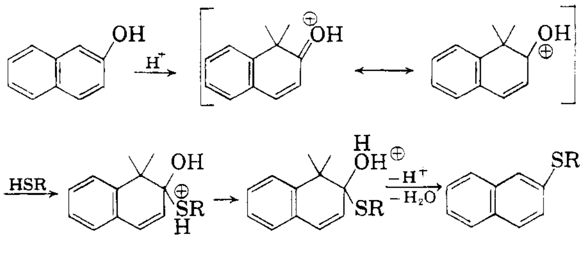


R = $-CH_3$	99% yield
$-C_2H_5$	68%
$-(CH_2)_4CH_3$	22%[3]
$-(CH_2)_{11}CH_3$	79%
$-CH_3COOH$	87%
$-C_6H_5$	43%[3]

1-Naphthol, 6-bromo-2-naphthol and 1,5-naphthalenediol reacted similarly with thioglycolic acid to yield the corresponding naphthylthioacetic acids.

No product was obtained in the absence of an acid catalyst. Toluenesulfonic acid and mixed alkanesulfonic acids were effective. Other catalysts which had activity were concentrated sulfuric acid, sodium bisulfate and polyphosphoric acid. The yields were lower if an appreciable amount of water was present.

This reaction, which is somewhat analogous to the Bucherer reaction, is another manifestation of the ability of naphthols to undergo attack by certain nucleophiles, such as methanol,[4] under acid catalysis and resembles formally the formation of a hemithioketal.



An alternative mechanism involves the attack of the mercaptan on the carbonium ion derived from 2-naphthol by protonation of the hydroxyl group and its loss as water. This may be the mechanism in case of compounds which form carbonium ions easily. For example, *s*-triphenyl-

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[1] This material was presented before the Organic Group of the North Jersey Section of the American Chemical Society Eleventh Annual Meeting in Miniature, South Orange, N. J., January 26, 1959.

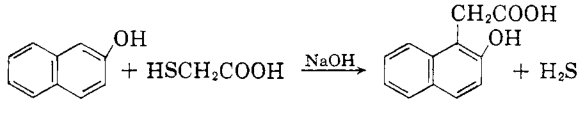
[2] W. B. Hardy, J. H. Thelin and F. M. Furman, U. S. Patent 2,884,449.

[3] These values represent purified yields from a single experiment and do not necessarily represent the optimum conditions.

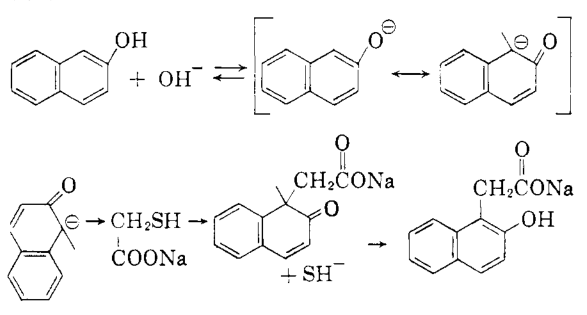
[4] L. Gattermann, *Ann.*, **244**, 72 (1888).

methylthioglycolic is obtained by heating triphenylcarbinol and thioglycolic acid in aqueous 2 *N* hydrochloric acid.[5,6] However, it seems unlikely that a naphthol would yield a carbonium ion under these experimental conditions.

The Alkaline-catalyzed Reaction.—Equimolar amounts of 2-naphthol, thioglycolic acid and 1.5 moles of sodium hydroxide were heated 23 hours at 145–150° in ethylene glycol. 2-Hydroxy-1-naphthaleneacetic acid was obtained in 89% yield. This procedure is more convenient and gives a higher yield than other direct methods for preparing this compound.[7,8]



One and one-half molar equivalents of sodium hydroxide was found to give optimum yields. A possible explanation of this alkaline-catalyzed reaction is[9]



The optimum base requirement is probably associated with a complex set of acid–base equilibria involving the mercaptan, naphthol and carboxyl functions. Also, the picture of the nucleophilic displacement is probably an oversimplification which ignores the neighboring group effects. For example, 3-mercaptopropionic acid reacted in the same way with 2-naphthol but the yield of 2-hydroxy-1-naphthalenepropionic acid was much lower.

Experimental

All melting points are uncorrected.

(2-Naphthylthio)-acetic Acid.—2-Naphthol (28.8 g., 0.20 mole), thioglycolic acid (20 g., 0.22 mole) and *p*-toluenesulfonic acid (10 g., 0.06 mole) were stirred for 16 hours at 115° under nitrogen. The reaction mixture was dissolved in 1,700 ml. of 1% sodium hydroxide solution at 60°. Carbon dioxide was bubbled into the solution until the *p*H was just alkaline. The precipitated solid was removed by filtration and discarded. The filtrate then was acidified with concentrated hydrochloric acid and the precipitated product was removed by filtration, washed with water and dried at 50°. A light gray solid, m.p. 89–91° (lit.[10] m.p. 91°), weighing 38 g. (87%) was obtained. A sample prepared in a similar manner was recrystallized from aqueous alcohol, m.p. 94–95°. *Anal.* Calcd. for $C_{12}H_{10}O_2S$: C, 66.1; H, 4.6; S, 14.7. Found: C, 65.8; H, 4.5; S, 14.9.

Experiments similar to the above showing the effect of various catalysts are found in Table I.

TABLE I

Catalyst	Yield, %
None	0
3 drops H_2SO_4	18
20 g. $NaHSO_4 \cdot H_2O$ + 10 ml. H_2O	17
20 g. $NaHSO_4 \cdot H_2O$	52
20 g. $NaHSO_4$ fused	69
3 ml. H_2SO_4	89
10 g. polyphosphoric acid	57
5 g. mixed alkanesulfonic acid	87

2-Naphthyl *n*-Dodecyl Sulfide.[11]—2-Naphthol (28.8 g., 0.2 mole), dodecanethiol (40.4 g., 0.2 mole), *p*-toluenesulfonic acid (10 g., 0.06 mole) and 5 ml. of toluene were stirred under nitrogen for 24 hours at 110°. The reaction product was washed with 200 ml. of water, 200 ml. of 2% NaOH and finally 200 ml. of water. The white solid, m.p. 39–45°, weighed 63 g. (96%). After recrystallization from 150 ml. of alcohol 52 g. (79%) of a white solid, m.p. 44–46°, was obtained. *Anal.* Calcd. for $C_{22}H_{32}S$: C, 80.4; H, 9.8; S, 9.8. Found: C, 80.2; H, 9.5; S, 9.6.

Other naphthyl sulfides were prepared in a similar manner and are shown in Table II.

2-Hydroxy-1-naphthaleneacetic Acid.—2-Naphthol (28.8 g., 0.2 mole), ethylene glycol (25 ml.), sodium hydroxide pellets (12.0 g., 0.3 mole) and thioglycolic acid (18.4 g., 0.2 mole) were stirred 23 hours at 145–150° under nitrogen. Hydrogen sulfide was continuously evolved. Water (175 ml.) was added and the mixture was stirred for two hours at 90°. The reaction mixture was diluted to two liters with water and the *p*H was made just alkaline to Brilliant Yellow indicator paper with hydrochloric acid. The solution was clarified at 60° and acidified with concentrated hydrochloric acid. The precipitated product was removed by filtration and washed with water. After drying at 50°, the white product, m.p. 151–152° (lit.[12] m.p. 147°), weighed 36.0 g. (89%). *Anal.* (of a similarly prepared sample, m.p. 149–150°) Calcd. for $C_{12}H_{10}O_3$: C, 71.2; H, 5.0. Found: C, 71.4; H, 5.0.

The mixture m.p. with 2-naphthoxyacetic acid was depressed. The lactone prepared by heating the acid at 140° for 5 minutes, and recrystallizing from alcohol and then hexane, had a melting point of 103–104° (lit.[12] m.p. 104°).

Another derivative, 2-methoxy-1-naphthaleneacetic acid, m.p. 210–212° (lit.[13] m.p. 210–211°), was prepared by allowing the acid to react with dimethyl sulfate in dilute alkali.

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[5] Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, Germany, 1955, Vol. IX, p. 117.

[6] B. Holmberg, *J. prakt. Chem.*, [2] **141**, 93 (1934).

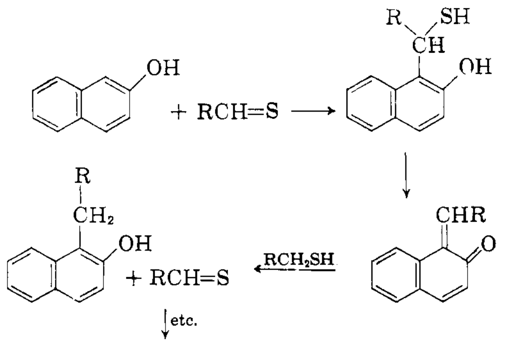
[7] C. O. Guss, THIS JOURNAL, **73**, 608 (1951).

[8] W. Griehl, *Chem. Ber.*, **80**, 410 (1947).

[9] One referee suggested an alternative mechanism which avoids the direct nucleophilic displacement of SH^- from carbon for which there is no analogy. The suggested mechanism is related to the known alkaline-catalyzed alkylation of 2-naphthol with methanol (J. W. Cornforth, R. H. Cornforth and R. Robinson, *J. Chem. Soc.*, 682 (1942)).

$$RCH_2SH + (\text{trace of oxidizing agent}) \rightarrow RCH{=}S$$
$$\text{or } RCH_2SH + (\text{trace of oxidizing agent}) \rightarrow RCH_2SSCH_2R$$
$$RCH_2SSCH_2R + \text{alkali} \rightarrow RCH{=}S + RCH_2SH$$

(then, in brief)



We feel that the reaction upon which this mechanism is based may not be comparable since (1) our temperature was lower, *e.g.* 150° *vs.* 220°; (2) our catalyst was milder, *e.g.* sodium hydroxide *vs.* sodium methoxide; (3) our yields were much higher; and (4) no reaction occurred when glycolic acid was substituted for thioglycolic acid under our conditions.

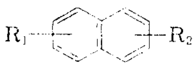
[10] P. Friedlander and N. Woroshzow, *Ann.*, **388**, 14 (1912).

[11] This compound was not found in the literature.

[12] R. Stoermer, *Ann.*, **313**, 91 (1900).

[13] F. Mauthner, *J. prakt. Chem.*, **95**, 59 (1917).

TABLE II



		Reactants			Iso- lation	Yield, %	M.p., °C.	Analyses, % Calcd./Found			
R_1	R_2	Naphthol	Mercaptan	Catalyst				C	H	S	Br
6-Br[11]	2-SCH_2COOH	6-Br, 2-OH (0.2 *m*)	$HSCH_2COOH$ (0.22 *m*)	TSA[h] (0.12 *m*)	[b]	91	163–165	48.5 48.6	3.0 3.1	10.8 10.9	26.9 26.6
H	1-SCH_2COOH	1-OH (0.2 *m*)	$HSCH_2COOH$ (0.22 *m*)	$NaHSO_4$ (0.15 *m*)	[b,d]	67	104–105 (111–112)[14]	66.1 65.8	4.6 4.7	14.7 14.7	
5-SCH_2COOH	1-SCH_2COOH	1,5-Diol (0.2 *m*)	$HSCH_2COOH$ (0.55 *m*)	TSA (0.12 *m*)	[b,e]	76	240–243 (250)[15]	54.5 54.6	3.9 4.0	20.8 20.9	
H[a]	2-SCH_3	2-OH (3.0 *m*)	CH_3SH (4.17 *m*)	TSA (0.87 *m*)	[c]	99	60–62 (63–64)[16]	Mixt. m.p. with known cmpd. not depressed[18]			
H[a]	2-SC_2H_5	2-OH (3.0 *m*)	C_2H_5SH (4.0 *m*)	TSA (0.87 *m*)	[c]	68	18–21 (16)[17]		..	..	
H[11]	2-$SC_5H_{11}(n)$	2-OH (0.2 *m*)	*n*-$C_5H_{11}SH$ (0.3 *m*)	TSA (0.06 *m*)	[c,f]	22[g]	16–17	78.4 78.2	7.8 7.5	13.9 14.2	
H	2-SC_6H_5	2-OH (0.2 *m*)	C_6H_5SH (0.25 *m*)	$NaHSO_4$ (0.17 *m*)	[c,d]	43[g]	50–51 (51.8)[19]	81.3 81.2	5.1 5.3	13.5 13.4	

[a] A 1.2-liter nickel autoclave was used. [b] The product was isolated in a manner similar to (2-naphthylthio)-acetic acid; hydrochloric acid was used instead of carbon dioxide to adjust the *p*H. [c] The product was isolated in a manner similar to 2-naphthyl *n*-dodecyl sulfide. [d] The product was recrystallized from alcohol. [e] The product was reprecipitated from alcohol with hydrochloric acid. [f] The product was recrystallized from hexane at −5–0° two times. [g] These are purified yields. [h] *p*-Toluenesulfonic acid.

The results of similar experiments with varying amounts of sodium hydroxide were: sodium hydroxide, 0.1 mole (18 hr.), 13% yield; 0.2 mole (23 hr.), 52% yield; 0.3 mole (23 hr.), 89% yield; 0.5 mole (24.5 hr.), 25% yield.

2-Hydroxy-1-naphthalenepropionic Acid.—2-Naphthol (28.8 g., 0.2 mole), ethylene glycol (25 ml.), sodium hydroxide pellets (12.0 g., 0.3 mole) and 3-mercaptopropionic acid (21.2 g., 0.2 mole) were stirred 17 hours at 150–170° under nitrogen. Hydrogen sulfide was evolved. The reaction mixture was diluted to one liter with water and clarified. The *p*H of the solution was made alkaline to Brilliant Yellow paper with hydrochloric acid. The precipitated 2-naphthol (10 g., 35%), was recovered by filtration. The filtrate was acidified and 15 g. of a tacky solid was removed by filtration (29% crude yield). Recrystallization from 1-butanol gave a white solid, m.p. 116–117° (lit.[20] m.p. 121°). The mixture m.p. with the known compound[20] was not depressed.

Acknowledgment.—The authors wish to thank Mr. O. E. Sundberg and his associates for the elemental analyses.

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[14] M. Schmidt to Kalle and Co., German Patent 414,853; *Frdl.*, **15**, 326 (1925).

[15] M. Schmidt and H. Rose to Kalle and Co., German Patent 380,712; *ibid.*, **14**, 927 (1923).

[16] F. Kehrmann and G. A. Sava, *Ber.*, **45**, 2898 (1912).

[17] F. Kroft and R. Schönherr, *ibid.*, **22**, 824 (1889).

[18] These compounds were prepared by the alkylation of 2-naphthalenethiol with dimethyl sulfate and diethyl sulfate. The 2-methylthionaphthalene melted at 60–61°. The 2-ethylthionaphthalene melted at 22–23°.

[19] E. Bourgeois, *Ber.*, **28**, 2327 (1895).

[20] A. F. Hardman, THIS JOURNAL, **70**, 2119 (1948).

BOUND BROOK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Synthesis of Derivatives of 1-Indanone and Indenone

BY HERBERT O. HOUSE, VASKEN PARAGAMIAN, ROLLAND S. RO[1] AND DAVID J. WLUKA[1]

RECEIVED JUNE 29, 1959

Synthetic routes to indenone ethylene ketal, 2-ethylideneindanone and 2-(2-carboxyethyl)-indenone have been developed. The dehydrobromination of 2-bromo-2-ethylindanone has been found to yield predominantly the exocyclic unsaturated ketone.

We have been led to study preparative routes to 2-substituted indenones since certain members of this series can serve as starting materials for the synthesis of degradation products of the plant-growth stimulant, gibberellic acid.[2] This paper reports the results of our preliminary studies in this area.

Several methods for the conversion of 1-indanone (I) to indenone have been studied,[3] the most successful method being the conversion of the indanone to 2-acetoxy-1-indanone and then pyrolysis. Since 1-indanone (I) could be converted in high yield either to 2-bromo-1-indanone (II) or 2,2-dibromo-1-indanone by direct bromination,[4] we were led to explore methods for the dehydrobromination of the monobromo compound II. Although no isolable product was obtained by direct reaction of the bromo ketone II with a variety of bases, conversion of the bromo ketone II to the ketal III followed by reaction with potassium *t*-butoxide afforded the unsaturated ketal IV in an over-all yield of 46%. The ketal IV, unlike its parent ketone,[3b] was stable on storage and could be used directly as a dienophile in Diels–Alder reactions.[5]

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[1] Alfred P. Sloan Postdoctoral Fellow.

[2] For leading references, see B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *Proc. Chem. Soc.*, 221 (1958).

[3] (a) R. Stoermer and E. Asbrand, *Ber.*, **64**, 2796 (1931); (b) C. S. Marvel and C. W. Hinman, THIS JOURNAL, **76**, 5435 (1954).

[4] (a) F. S. Kipping, *J. Chem. Soc.*, **65**, 501 (1894); (b) W. S. Johnson and W. E. Shelberg, THIS JOURNAL, **67**, 1745 (1945); (c) C. L. Arcus and G. C. Barrett, *J. Chem. Soc.*, 2740 (1958).

[5] H. O. House, V. Paragamian, R. S. Ro and D. J. Wluka, THIS JOURNAL, **82**, 1457 (1960).