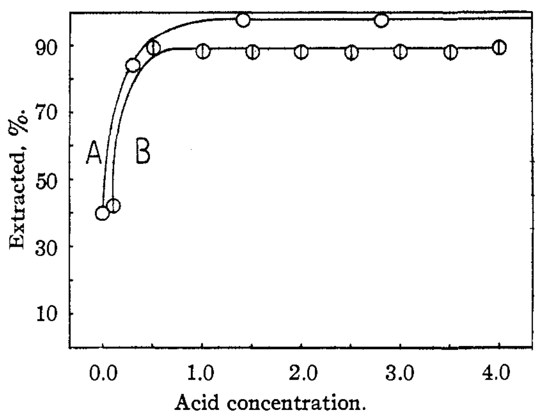

Fig. 2.—Percentage of gold extracted into diethyl ether as a function of hydrochloric acid concentration: curve A, literature values for 2×10^{-2} *M* gold; curve B, tracer gold.

be an effect dependent upon the total surface area. Increasing the available surface by the addition of silica increased the amount of adsorption but had no appreciable effect upon the shape of the adsorption curve as shown in Fig. 3. The peak in the adsorption curve at a *p*H value of about 2 might be explained by a consideration of the adsorbing species and the charge on the silica. In acid solutions the charge on the silica is probably positive due to adsorption of hydrogen ions and the adsorbing species could be the tetrachloroaurate(III) ion. At *p*H values lower than 2, the dissociation of tetrachloroauric(III) acid is less, and at *p*H values higher than 2, the silica has less of a positive charge, probably even becoming negative in the basic region. Also it should be recognized that the tetrachloroaurate(III) ion would tend to change into various chlorohydroxoaurate(III) ions as the solution becomes basic, but this would not alter the negative charge of the complex ion. The adsorption on Norit A carbon was found to be almost independent of the *p*H; however, it should be noted that the carbon tended to buffer solutions originally between a *p*H of 4.0 and 9.0 to a final *p*H of 7.5. The results of these experiments are given in Table III. It seems possible to explain the adsorption on carbon by the reduction of the gold(III) to the metallic form by the carbon, as has been reported for macroconcentrations of gold.[10]

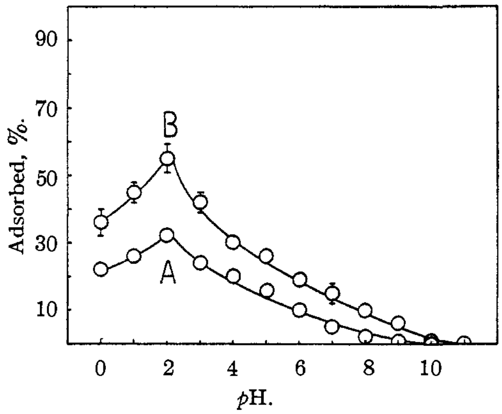

Fig. 3.—Percentage of gold adsorbed onto glass and silica from tracer gold solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H: curve A, adsorption on container and two glass beads; curve B, adsorption on container, two glass beads, and 100 mg. of silica.

TABLE III

ADSORPTION OF TRACER GOLD ONTO NORIT A CARBON[a]

*p*H		Adsorbed,	*p*H		Adsorbed,
Original	Final	%	Original	Final	%
0.0	0.0	97 ± 2	6.0	7.5	94 ± 2
1.0	1.0	97 ± 2	7.0	7.5	94 ± 2
2.0	2.0	96 ± 2	8.0	7.5	94 ± 2
3.0	3.0	95 + 3	9.0	7.5	93 ± 2
4.0	7.5	94 ± 2	10.0	10.0	93 ± 4
5.0	7.5	94 ± 2	11.0	11.0	93 ± 2

[a] Solutions originally 0.01 *N* in hydrochloric acid.

Acknowledgment.—The authors wish to express their gratitude to the United States Atomic Energy Commission for the grant which supported this research.

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[10] O. Ruff, F. Ebert and F. Luft, *Z. anorg. allgem. Chem.*, **170**, 49 (1929); H. Wohling, *Z. angew. Chem.*, **45**, 720 (1932); V. E. Heymann, K. Solomon and H. Kieffer, *Z. anorg. allgem. Chem.*, **187**, 97 (1930).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TENNESSEE
KNOXVILLE 16, TENNESSEE

A Derivative of a New Sulfur Heterocycle[1]

BY GEORGE P. SCOTT

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Recent research on azulenes, tropolones and cycloöctatetraene has indicated wide-spread interest in large ring compounds containing aromatic or pseudo-aromatic structures. This report describes the preparation of a compound which very probably contains a sulfur atom in a seven-membered ring involving a system of double bonds formally analogous to the thiophene system.

The diethyl ester of thiodiacetic acid was condensed with *o*-phthalaldehyde using a sodium methoxide catalyst as in the Hinsberg thiophene synthesis.[2,3] Upon acidification of the precipitated sodium salt, an impure, orange, crystalline acid was obtained. Although very unstable in solution, it was found possible to recrystallize it rapidly from hot, 80% ethanol containing a little hydrochloric acid. The analysis and neutral equivalent of the resulting product corresponded to 3-benzothiepin-2,4-dicarboxylic acid[4](I).

Because of the instability of this compound, attempts to prepare simple acid derivatives and reduction products have failed. Refluxing in 15% ethanol produced a white, crystalline, sulfur-free acid in high yield (95%). This was identified as 2,3-naphthalenedicarboxylic acid (II) by analysis and mixed melting point of its anhydride.

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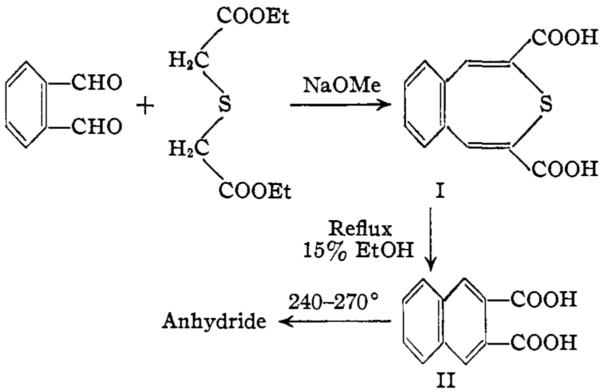
[1] This work was aided by a grant from the Research Corporation.

[2] D. E. Wolf and K. Folkers, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 435.

[3] For comparable carbon ring syntheses see D. S. Tarbell, G. P. Scott and A. D. Kemp, THIS JOURNAL, **72**, 379 (1950); L. F. Fieser and M. M. Pechet, *ibid.*, **68**, 2577 (1946); J. Thiele and E. Weitz, *Ann.*, **377**, 1 (1910).

[4] Nomenclature and numbering is based upon the *Chemical Abstracts* system, A. M. Patterson, L. T. Capell and M. A. Magill, *C. A.*, **39**, 5889 (1945).



Although the structure of the initial condensation product is not rigorously proven, its method of formation and the result of the decomposition make its identity with structure I exceedingly probable. Its instability with respect to the highly resonant naphthalene derivative is in accord with the observation that a Fisher–Taylor–Hirschfelder model of this structure is somewhat strained and definitely not planar. The ultraviolet absorption spectrum in absolute ethanol showed a peak at 280 mμ; however, the apparent molar absorption coefficient at this wave length decreased continuously indicating decomposition at room temperature. It is planned to study this decomposition further.

Experimental[5]

Condensation of *o*-Phthalaldehyde with Diethyl Thiodiacetate.—A solution of 9.00 g. (0.0437 mole) of the ester and 5.85 g. (0.0437 mole) of the aldehyde in 15 ml. of absolute methanol was run into a solution of sodium methoxide made by dissolving 4.2 g. of metallic sodium in 60 ml. of methanol. The solution was stirred and cooled, and the rate of addition was regulated so that the temperature did not rise above 15°. The mixture was allowed to stand in an ice-bath for an additional two hours and was evaporated at room temperature by suction to a volume of about 40 ml. After dissolving the yellowish precipitate by adding about 90 ml. of cold water, the solution was immediately acidified by dropwise addition of excess cold 18% hydrochloric acid while stirring vigorously in an ice-bath. The orange solid which precipitated amounted to 5.7 g., but it was not completely fusible up to 305° indicating that it contained some unchanged sodium salt.

Recrystallization was accomplished in two equal portions by adding each portion to 200 ml. of boiling 80% ethanol and stirring rapidly for 20 or 30 seconds. Concentrated hydrochloric acid (4 ml.) was then added and the solutions stirred again. Without waiting for the last bits of solid to dissolve, the solutions were poured through fast filter paper (without suction) into flasks cooled in an ice-bath. After allowing the filtrate to stand one-half hour in a refrigerator, the product was collected and dried. It consisted of fine, uniform, orange needles which were soluble in 5% sodium bicarbonate solution. It appeared stable for weeks in a desiccator; however, it was found that further recrystallization tended to produce a less pure product. Upon heating it sintered and turned nearly white at 185–195° and then melted with effervescence at 236.0–237.5°. The total yield was 2.4 g. (22%).

Anal. Calcd. for $C_{12}H_8O_4S$: C, 58.05; H, 3.25; S, 12.92; neut. equiv., 124. Found: C, 58.30; H, 3.46; S, 13.05; neut. equiv., 126.

Decomposition of the Condensation Product.—A sample of the above product (1.001 g.) was refluxed with about 50 ml. of 15% ethanol for two hours. Upon cooling, the solid, which had turned nearly white during the first 20 minutes, was filtered. A small second crop was obtained by evaporating the filtrate to a volume of 5 ml. The combined precipitates were then heated to boiling and agitated with 10 ml. of 10% sodium carbonate solution. After cooling the mixture, a quantity (113 mg.) of nearly white solid was removed by filtration. This evidently contained most of the sulfur; it was soluble in carbon disulfide and burned with a pale blue flame producing sulfur dioxide; however, it appeared to differ from the common crystalline forms of free sulfur (m.p. 115–118).

Acidification of the filtrate yielded 832 mg. of a white, crystalline, sulfur-free acid (m.p. 236.5–237.5° with effervescence). By recrystallization from water–dioxane mixture, the melting point was raised to 237.5–238.5°. Sublimation at atmospheric pressure and 240–270° temperature yielded the anhydride (m.p. 245–246 with some previous sublimation).

Anal. Calcd. for $C_{12}H_6O_3$: C, 72.73; H, 3.05. Found: C, 72.82; H, 3.31.

It produced no depression of the melting point when mixed with 2,3-naphthalenedicarboxylic anhydride prepared from 3-amino-2-naphthoic acid by the method of Waldman and Mathiowetz.[6]

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[5] Microanalyses are by Clark Microanalytical Laboratory, Urbana, Illinois. Melting points are corrected.

[6] H. Waldman and H. Mathiowetz, *Ber.*, **64**, 1713 (1931).

Department of Chemistry
University of South Dakota
Vermillion, South Dakota

Alkylation with Long Chain *p*-Toluenesulfonates. VI. Friedel–Crafts Reaction of *n*-Octadecyl *p*-Toluenesulfonate and Benzene[1]

By David A. Shirley[2] and Joseph R. Zietz, Jr.

Received August 10, 1953

In 1928 Clemo and Walton[3] observed the alkylation of benzene with simple alkyl *p*-toluenesulfonates in the presence of aluminum chloride. A patent was issued to Foldi[4] in 1933 involving this general type reaction.

As a part of a general program of evaluation of the alkylating properties of long chain *p*-toluenesulfonates[5] we examined the reaction of *n*-octadecyl *p*-toluenesulfonate with benzene in the presence of aluminum chloride. An 73% yield of *n*-octadecylbenzene was obtained. The lack of apparent rearrangement in the long chain fragment is in line with an observation of Gilman and Turck[6] in the Friedel–Crafts alkylation of benzene with *n*-octadecyl bromide.

This note concludes our work on alkylation reactions of long chain *p*-toluenesulfonates.

Experimental

Benzene (156 g. or 2.0 moles) was dried by distilling off 39 g. (0.5 mole) and 42.5 g. (0.10 mole) of *n*-octadecyl *p*-toluenesulfonate[7] was added followed by 13.3 g. (0.10 mole) of aluminum chloride. The mixture was stirred at room temperature for 15 hours, for 10 hours at 50–55° and for a final 14 hours at room temperature. The deep orange-colored reaction mixture was poured into excess ice–hydrochloric acid mixture. The organic layer was separated and washed with warm dilute hydrochloric acid, dried over calcium chloride and distilled to remove benzene. The residue

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[2] Department of Chemistry, University of Tennessee, Knoxville, Tennessee.

[3] G. R. Clemo and E. Walton, *J. Chem. Soc.*, **133**, 723 (1928).

[4] Z. Foldi, U. S. Patent 1,897,795; *C. A.*, **27**, 2693 (1933).

[5] Preceding paper, D. A. Shirley and J. R. Zietz, Jr., *J. Org. Chem.*, in press.

[6] H. Gilman and J. A. V. Turck, This Journal, **61**, 478 (1939).

[7] D. A. Shirley and W. H. Reedy, *ibid.*, **73**, 458 (1951).