was added dropwise over a period of 15 min. to a mixture of 6-nitro-3-indolealdehyde (1.00 g., 0.00520 mole) and acetic acid (200 cc.). The light yellow solution turned dark brown and all of the 6-nitro-3-indolealdehyde dissolved. The solution was stirred at room temperature for 30 hr., during which time a bright orange solid precipitated. The solid (0.37 g., 0.00193 mole, 37%), m.p. 287–290°, was filtered, washed with water, dried, and recrystallized three times from 95% ethanol, yielding 6-nitroisatin as a mixture of dark orange needles and light yellow fluffy solid, m.p. 288–290° dec.; reported[5] m.p. 288–290° dec.; λ_{max} mμ (log ϵ) in 95% C_2H_5OH: 239 (4.37), 272 infl. (3.85), 339 infl. (3.20), 395 diffuse infl. (3.06); ν_{NH} 3150 m, $\nu_{C=O}$ 1750 s infl., 1741 s, 1711 ms, 1624 s, ν_{NO_2} 1550 s, and 1360 ms or 1335 s cm.$^{-1}$ in Nujol.

Anal. Calcd. for $C_8H_4N_2O_4$ (192.13): C, 50.01; H, 2.10; N, 14.58; C, 50.04; H, 2.29; N, 14.77.

The acetic acid mother liquor was diluted with water (600 cc.) and extracted with ether (6 × 100 cc.). Evaporation of the ether extracts left an orange-brown solid (0.2 g., 0.00104 mole, 20%). One recrystallization from 95% ethanol gave a sample, m.p. 263–273°, shown by its infrared spectrum in Nujol to be 6-nitroisatin contaminated by 6-nitro-3-indolealdehyde starting material.

4-Nitroanthranilic Acid (V). A. By Hydrolysis of *N*-Acetyl-4-nitroanthranilic Acid.—A solution of *N*-acetyl-4-nitroanthranilic acid[8] (1.00 g., 0.00446 mole) and 6 *N* hydrochloric acid (50 cc.) was refluxed for 1.5 hr. The cooled solution was extracted with ether (3 × 125 cc.), and the ether extracts were dried over anhydrous magnesium sulfate and evaporated, leaving a bright orange solid. Recrystallization from 95% ethanol yielded bright orange needles (0.55 g., 0.00302 mole, 68%), m.p. 266–268° dec.; reported: m.p. 263–264°[7a], 264°,[7b] 269°[7c]; ν_{NH} 3460 m, 3360 m, $\nu_{C=O}$ 1683 s, ν_{NO_2} 1528 s, 1362 ms cm.$^{-1}$ in Nujol.

B. By Oxidation of 6-Nitroisatin.—The procedure is essentially that used previously for oxidation of 5-nitroisatin to 5-nitroanthranilic acid.[6] 6-Nitroisatin (0.13 g., 0.00068 mole) was dissolved in aqueous 10% sodium hydroxide solution (5 cc.), 3% hydrogen peroxide solution (4.3 cc.) was added, and the solution was kept at room temperature for 30 min. The solution was filtered through a sintered glass funnel and acidified to *p*H 1 with concd. hydrochloric acid, causing precipitation of a heavy yellow solid (0.11 g., 0.00060 mole, 88%), m.p. 263–266° dec. A mixed melting point with the sample prepared by acid hydrolysis of *N*-acetyl-4-nitroanthranilic acid (see part A, above) was undepressed, and the infrared spectra in Nujol were identical.

Ethyl 3-Indolecarboxylate was prepared by a Grignard coupling reaction from indolemagnesium iodide and ethyl chloroformate.[2,10,11] After elution from alumina with ethyl acetate and three recrystallizations from ethanol–water, our sample had a melting point, 126–127°,[12] higher than the 118–119° reported;[10] λ_{max} mμ (log ϵ) in 95% C_2H_5OH: 213 (4.56), 242 infl. (3.97), 281 (4.06), 286 (4.04); ν_{NH} 3450 m, 3300 m in $CHCl_3$, 3240 ms in Nujol, $\nu_{C=O}$ 1678 s in $CHCl_3$, 1685 m, 1661 s cm.$^{-1}$ in Nujol.[12]

Ethyl 6-nitro-3-indolecarboxylate was prepared in 6% yield by nitration of ethyl 3-indolecarboxylate in acetic acid by the method of Majima and Kotake,[2] who did not state the yield. The product, obtained by elution from alumina and recrystallization from ethanol-water, had a melting point of 200–201°; reported m.p. 198–199°;[2] λ_{max} mμ (log ϵ) in 95% C_2H_5OH: 270 (4.16), 320 (3.72), 329 infl. (3.68); ν_{NH} 3230 m, $\nu_{C=O}$ 1692 s infl., 1679 s, ν_{NO_2} 1521 s, 1349 s cm.$^{-1}$ in Nujol.

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[10] R. Majima and M. Kotake, *Ber.*, **55**, 3865 (1922).

[11] We are indebted to Daryl L. Ostercamp for this preparation.

[12] Donald N. Robinson, Ph.D. thesis, Univ. of Minnesota, March, 1959, p. 129.

Sodium Triphenylgermanethiol. Synthesis of Some New Organothiogermanes

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Only a few organogermanium compounds have been synthesized which contain germanium directly linked to sulfur. Of this type the following have been prepared: R_3GeSR,[2a] R_2GeS,[2b] $(RS)_4Ge$,[3a] $(RS)_3GeX$,[3b] $R_3GeSSGeR_3$,[4] $(R_3Ge)_2S$,[4] and $(R\text{-}GeS)_2S$.[5]

Gilman and Lichtenwalter[6] have reported the synthesis of lithium triphenylsilanethiol in tetrahydrofuran solution by treating triphenylsilyllithium with elemental sulfur. Proof of its existence was established by reaction with several RX type compounds. Solutions of triphenylgermyllithium[7] do not react as smoothly with elemental sulphur as the corresponding silyllithium compound.

The sodium salt of triphenylgermanethiol, on the other hand, may be prepared and isolated in good yields after dropwise addition of a benzene solution of triphenylbromogermane to a freshly prepared suspension of sodium sulfide in ethanol:

$$(C_6H_5)_3GeBr + Na_2S \longrightarrow (C_6H_5)_3GeSNa(I) + NaBr$$

The pure salt (I), although hygroscopic, has been stored in a dessicator containing Drierite for over a month without change. It is soluble in benzene, alcohol, and water. An aqueous solution, alkaline to *p*H paper, becomes turbid after several minutes with the liberation of a hydrogen sulfide-like odor. Refluxing in commercial anhydrous alcohol produces bis(triphenylgermanium) sulfide and sodium sulfide. The reaction is reversible since bis(triphenylgermanium) sulphide when refluxed with excess sodium sulfide produces starting material (I):

$$(C_6H_5)_3GeSNa \underset{XS.Na_2S}{\overset{C_2H_5OH}{\rightleftharpoons}} (C_6H_5)_3GeSGe(C_6H_5)_3 + Na_2S$$

The reaction of I with RX type compounds presents a convenient method for the synthesis of sulfur containing organogermanium compounds, Table I:

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[1] Research Fellow sponsored by the Germanium Research Committee.

[2] (a) H. H. Anderson, *J. Org. Chem.*, **21**, 869 (1956). (b) *J. Am. Chem. Soc.*, **78**, 1692 (1956).

[3] (a) H. J. Backer and F. Stienstra, *Rec. trav. chim.*, **52**, 1033 (1933), **54**, 607 (1935). (b) **54**, 38 (1935).

[4] R. Burschkies, *Ber.*, **69**, 143 (1936).

[5] H. Bauer and R. Burschkies, *Ber.*, **65**, 956 (1932).

[6] H. Gilman and G. Lichtenwalter, *J. Org. Chem.*, **25**, 1064 (1960).

[7] H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).

TABLE I

REACTIONS OF $(C_6H_5)_3GeSNa$

Compound No.	RX	Product	Yield, %	M.P.	Formula	Found C	Found H	Found Ge	Found S	Calcd. C	Calcd. H	Calcd. Ge	Calcd. S
II	CH_3I	(Methylthio)triphenylgermane	62	87–88	$C_{19}H_{18}GeS$	64.88	5.30	20.50	9.24	65.10	5.16	20.70	9.14
III	n-C_4H_9I	(n-Butylthio)triphenylgermane[a] ·	70	147–150/0.05 mm.	$C_{22}H_{24}GeS$	66.92	6.16	18.62	7.55	67.30	6.16	18.48	8.15
IV	$C_6H_5CH_2Cl$	(Benzylthio)triphenylgermane	59	98.5	$C_{25}H_{22}GeS$	69.92	5.32	17.05	7.55	70.30	5.19	17.00	7.51
V	$C_6H_5C(O)Cl$	(Benzylthio)triphenylgermane	67	145.5	$C_{25}H_{20}GeOS$	67.80	4.69	16.49	7.18	68.10	4.51	16.47	7.26
VI	p-$NO_2C_6H_4C(O)Cl$	(p-Nitrobenzoylthio)triphenylgermane	58	151	$C_{25}H_{19}GeNO_3S$	61.40	4.01	14.80	6.90	61.70	3.95	14.95	6.60
VII	$(C_6H_5)_3GeBr$	Bis(triphenylgermanium) sulfide[b]	67	138.5	$C_{36}H_{30}Ge_2S$								
VIII	CH_3SCH_2Cl	[(Thiomethyl)methylthio]triphenylgermane	65	63.0	$C_{20}H_{10}GeS$	60.35	5.15	18.24	16.30	60.40	5.08	18.28	16.15
IX	CH_3SO_2Cl	Bis(triphenylgermanium) disulfide	50	171–172	$C_{36}H_{30}Ge_2S_2$	63.90	4.55	21.40	9.31	64.20	4.50	21.60	9.55
X	$(C_6H_5)_2GeBr_2$	Diphenyl(bistriphenylgermanethio)germane	52	162	$C_{48}H_{40}Ge_3S_2$	64.19	4.51	24.15	7.11	64.20	4.48	24.25	7.14

[a] Liquid with refractive index = 1.6135. [b] Known compound. Identified by mixed melting point + comparison of infrared spectrum.

$$(C_6H_5)_3GeSNa + RX \longrightarrow (C_6H_5)_3GeSR$$

R = $-CH_3$ (II); $-n$-C_4H_9 (III); $-CH_2C_6H_5$ (IV); $-C(O)C_6H_5$ (V); $-C(O)C_6H_4NO_2$-p (IV); $-Ge(C_6H_5)_3$ (VII); $-CH_2SCH_3$ (VIII)

Carbon disulfide treated with I and methyl iodide did not produce the expected organogermane substituted carbonic acid trithioester. Instead bis(triphenylgermanium) sulfide and disodium trithiocarbonate were formed. It is not clear whether the expected reaction A took place and subsequently, through decomposition, formed bis(triphenylgermanium) sulfide and disodium trithiocarbonate or whether I is unstable in carbon disulfide solution. In the later case, reaction B, the initially formed sodium sulfide could have reacted with carbon disulfide to form the sodium trithiocarbonate.[8] Reaction of I with methanesulfonyl chloride forms the symmetrical disulfide and not the thiosulphonyl compound in a manner similar to that described for the synthesis of organic disulfides[9]:

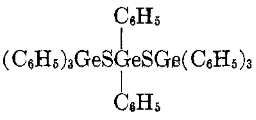
$$2(C_6H_5)_3GeSNa +$$

$$\begin{tikzcd}
CS_2 \arrow[r, "A"] \arrow[d, "B"] & {[2(C_6H_5)_3GeSC(S)SNa]} \arrow[r] & {[(C_6H_5)_3Ge]_2S + Na_2SC_3} \\
{} & {[(C_6H_5)_3Ge]_2S + Na_2S} \arrow[ur, "CS_2"] &
\end{tikzcd}$$

$$2(C_6H_5)_3GeSNa + CH_3SO_2Cl \longrightarrow$$
$$(C_6H_5)_3GeSSGe(C_6H_5)_3 \text{ (IX)} + NaCl + RSO_2Na$$

When two equivalents of I reacted with one equivalent of diphenyldibromogermane the expected diphenyl(bistriphenylgermanethio)germane (X) was isolated in good yield:

$$2(C_6H_5)_3GeSNa + (C_6H_5)_2GeBr_2 \longrightarrow$$



$$(C_6H_5)_3GeS\underset{C_6H_5}{\overset{C_6H_5}{Ge}}SGe(C_6H_5)_3$$

(X)

Experimental[10]

Preparation of the Sodium Salt of Triphenylgermanethiol (I).—Excess sodium sulfide pentahydrate, 10 g. (71 mmoles), recrystallized from ethanol, was suspended in 130 ml. of absolute ethanol at room temperature. Triphenylbromogermane, 10 g. (26 mmoles), dissolved in 70 ml. of benzene, was added dropwise over a 10-min. period while stirring. After 15-min. of additional stirring the solution was filtered, the clear solution evaporated to dryness and the resulting white crystalline mass extracted with benzene. Filtration removed the excess sodium sulfide and bromide. The filtrate was evaporated yielding 9 g. of product. This material was dissolved in benzene at approximately 50° and 80 ml. of hexane added. Within minutes white crystals formed which, after filtration, were washed with hexane and vacuum dried

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[8] E. Emmett Reid, "Organic Chemistry of Bivalent Sulphur," Vol. I, Chem. Publ. Co., Inc., New York, 1958. p. 31.

[9] D. T. Gibson, C. J. Miller, and S. Smiles, *J. Chem. Soc.*, **127**, 1821 (1925).

[10] Melting points were determined with a Kofler hot stage. Infrared spectra of all organogermanium compounds, in addition to the normal absorptions, contained the characteristic phenyl-germanium absorption at 9.15 μ, J. G. Noltes, M. C. Henry, and M. J. Janssen, ***Chem. Ind.*** (London), 1959, 298.

to yield 8.2 g. (88%) of the sodium salt of triphenylgermanethiol (I), m.p. 185–195°. The melting point could not be improved by recrystallization.

Anal. Calcd. for $C_{18}H_{15}GeSNa$: Na, 6.45; Found: Na, 6.34.

Typical Reaction Conditions.—A solution of the RX compound (5.8 mmoles) in 10 ml. of benzene was added slowly to a solution of 2.0 g. (5.8 mmoles) of the sodium salt (I) and the mixture stirred for 3 hr. The white precipitate of sodium halide that formed during the reaction was filtered and washed with 2 ml. of benzene. The filtrate was evaporated in vacuum and the crude product recrystallized from hexane.

Reaction of I with Carbon Disulfide.—A 2.0-g. sample (5.8 mmoles) of I was dissolved in 50 ml. of carbon disulfide. The clear solution slowly formed an orange precipitate. After 10 days the mixture was filtered. The yield was 600 mg. The orange-colored compound turned red in moist air, was insoluble in benzene and soluble in water.

Evaporation of the filtrate and recrystallization from hexane yielded 1.3 g. of long, white needles, m.p. 138°, bis-(triphenylgermanium) sulfide identified by infrared spectra and mixed melting point using a known sample.

The orange compound (250 mg.) was refluxed with 0.2 ml. of methyl iodide in 30 ml. of benzene for 5 hr. during which time the benzene solution became yellow and a precipitate (400 mg.) of sodium iodide formed. The benzene was evaporated leaving a strong smelling, yellow oil (150 mg.). The mass spectral pattern indicates a molecular weight of 136. This information together with the infrared spectrum tentatively suggests this compound to be dimethyl trithiocarbonate.

Acknowledgment.—The authors are grateful to C. DiPietro of the analytical laboratory of this division for the microanalyses.

The Reaction between 2-Nitro-1-phenylpropene and Cyclohexanone

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Commercial Solvents Corp., Terre Haute, Ind.

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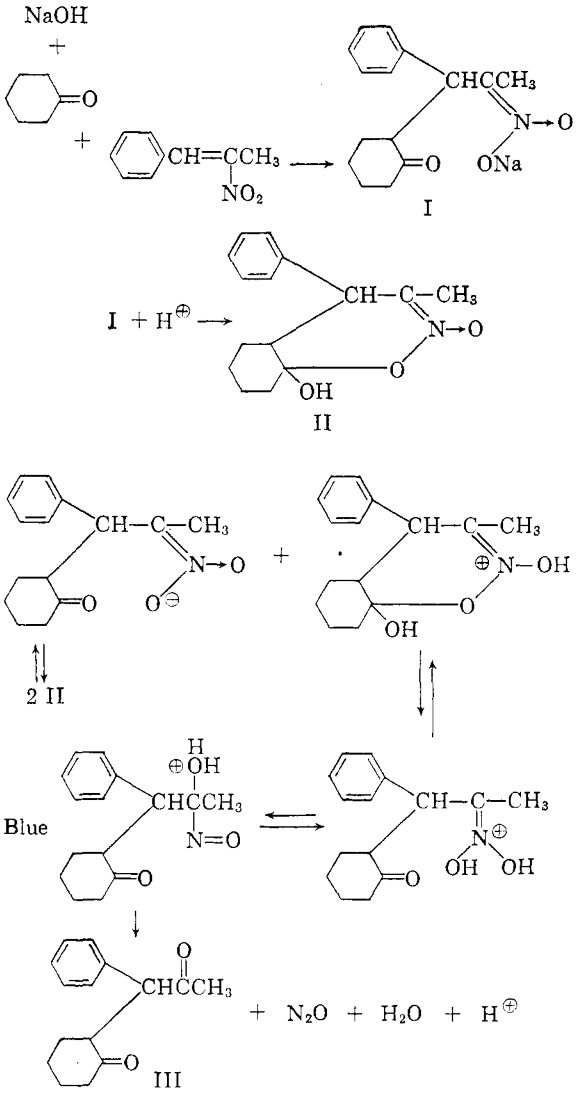
In an attempt to prepare a nitro ketone desired for synthetic work an aqueous solution of one equivalent of sodium hydroxide was added to a solution of one equivalent of 2-nitro-1-phenylpropene in excess cyclohexanone. Upon stirring, a sharp temperature rise occurred and the mixture became one phase. Addition to methanol containing an excess of acetic acid led to a crystalline precipitate which has an analysis corresponding to the expected nitro ketone, but which is now believed to be the cyclic condensation product II.

Compound II melts with decomposition, is only slightly soluble in organic solvents or water, but dissolves readily in aqueous sodium hydroxide. The infrared spectrum is complex, but strong bands are absent from the regions around 1700 cm.$^{-1}$, 1540 cm.$^{-1}$, and 1350 cm.$^{-1}$ where intense bands would be expected from a nitro ketone. Of interest are strong bands at 1615 cm.$^{-1}$ and 3145 cm.$^{-1}$, which we interpret as evidence for a ring C=N,[1] and a hydroxyl group, respectively.

Refluxing II in methanol leads to the development of a blue color, the evolution of nitrous oxide, and finally, to the formation of a crystalline product containing no nitrogen, showing strong carbonyl absorption, and giving the correct analysis for the 1,4-diketone III. Further evidence for the 1,4-diketone structure is the reaction of III with aniline which gives a compound having a nitrogen analysis corresponding to the expected 4,5,6,7-tetrahydroindole.

On dissolving compound II in aqueous sodium hydroxide and adding this solution to a large excess of acetone a crystalline sodium salt forms (as a hexahydrate) which shows strong absorption in the carbonyl region of the infrared spectrum. Reaction of this sodium salt with bromine gives a bromo nitro ketone, while reaction with benzyl chloride gives sodium chloride, a strong odor of



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[1] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955), found a band for the C=N at 1625–1600 cm.$^{-1}$ in the furoxan ring.