wt., 479. Found: C, 65.45; H, 7.65; mol. wt. 268, 283 (Rast, camphor), 400 (ebullioscopic, butanone).

"Entrainment" Reactions Involving Halosulfones, Magnesium and Ethyl Bromide.—About one-seventh of a solution of 17.7 mmoles of V and 18.0 mmoles of ethyl bromide in 35 ml. of ether was added to 35.4 m. atoms of magnesium and 0.1 g. of catalyst.[36] After reaction began, the remaining solution was added with stirring during 40 minutes. Considerable white precipitate appeared, which slowly became gummy. The mixture was stirred for 2 hours and heated under reflux for 15 minutes. Benzaldehyde[24] (37.4 mmoles) in 15 ml. of ether was added, and the product isolated and recrystallized[4]; yield of III, 2.72 g. (59%), m.p. 91.5–95°. Further recrystallization gave III with m.p. (constant) and mixture[4] m.p. of 93–94°.

The ether solution from the reaction of ethyl bromide and VIII (7.7 mmoles each) with magnesium (15.4 m. atoms) gave no color test[21] and 8.2 m. atoms of metal was recovered, thus indicating that VIII reacted with ethylmagnesium bromide formed rather than with magnesium. In order to confirm the probability of an addition reaction, ethereal ethylmagnesium bromide (70.4 mmoles) was added to VIII (12.96 g., 56.2 mmoles) in 100 ml. of ether during 0.75 hour at about −15°. A gum appeared and the clear solution gave a negative color test.[21] The mixture was stirred at 5° for 2 hours and then at 25°. Since negligible gas was evolved, the reaction evidently involved no "active" hydrogen atoms. A benzene extract of the acidified product contained negligible amounts of *p*-toluenesulfinic acid; hence cleavage of VIII was insignificant. The sirup (12.42 g.) obtained from the extract was shaken with 5% aqueous potassium permanganate until decolorization ceased (145 ml.). The saturated residue (8.1 g.) upon distillation at 98–100° (0.01 mm.) yielded 3.80 g. of colorless oil, $n^{25}\text{D}$ 1.5308–1.5311, which contained no chlorine. *Anal.* C, 64.49; H, 7.70; S, 11.47; nitro derivative[39] (547.9 mg., m.p. 63–64°, from 667.3 mg.), constant m.p. 65.5–66°. *Anal.* C, 53.61, 53.46; H, 5.45, 5.72; N, 5.16; mol. wt., 186, 191 (Rast in camphor), 433, 482 (ebullioscopic, in butanone). A similar reaction probably also occurred with IX but the product was intractable.

Reaction of X and ethyl bromide (11.7 mmoles each) with magnesium (23.6 m. atoms) and 0.2 g. of catalyst[36] yielded oil from which only 21% of X was recovered; the residue decolorized aqueous potassium permanganate. Similarly, reaction of XI (9.6 mmoles) and ethyl bromide (10.4 mmoles) with magnesium (19.5 m. atoms) and catalyst[36] yielded XI (26%) and a little halogen-free unsaturated material, m.p. 62–64° (probably vinyl *p*-tolyl sulfone); in a similar experiment at least 50% of one molar equivalent of gas was evolved and, after addition of benzaldehyde, the only isolable materials were traces of XI and *p*-toluenesulfinic acid, and 85% of the magnesium taken in excess of ethyl bromide. XIII reacted with ethyl bromide and magnesium (7 hours in refluxing ether) but, although titration[37] indicated basic magnesium in 35% yield (a negative color test[21] indicated negligible ethylmagnesium bromide), recovery of 81% of metal in excess of ethyl bromide and evidence for several organic products suggest that side reactions probably greatly exceeded any useful conversion to a Grignard reagent.[40]

Precipitation of Diphenyl Sulfone by Ethylmagnesium Bromide.—When 3.3 mmoles of 3.43 *N* ethereal ethylmagnesium bromide was added to 6.5 mmoles of dry diphenyl sulfone in 100 ml. of ether, a flocculent precipitate appeared which soon became gummy. Centrifugation, washing under nitrogen with two 25-ml. portions of benzene, and drying to constant weight resulted in 219.8 mg. of gummy solid, which upon titration[37] evolved gas and proved equivalent to 1.1 mmoles of basic magnesium. Filtration of the chilled solution then yielded 51.5 mg. of diphenyl sulfone, m.p. 124–128° (undepressed by authentic material). A duplicate experiment, except for omission of the sulfone, resulted only in 10.1 mg. of precipitate (probably in consequence of slight hydrolysis during manipulation).

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(39) V. N. Ipatieff and B. S. Friedman, THIS JOURNAL, **61**, 684 (1939).

(40) It is worth noting that the activity of V and the inactivity of X, XI and XIII in entrainment conversions support the suggestion that reactivity of a halogen atom with Grignard reagents may be expected if the hydrogen atom which it replaces is "active" toward Grignard reagents (ref. 15, p. 1062).

NASHVILLE 5, TENN.

[CONTRIBUTION FROM THE SCHOOL OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

2-Phenylselenosemicarbazide and Related Compounds. Dipole Moment and Spectroscopic Measurements on Analogous Ureides, Thioureides, and Selenoureides[1,2]

BY HENRY G. MAUTNER[3] AND W. D. KUMLER

RECEIVED JULY 18, 1955

2-Phenylselenosemicarbazide, its sulfur and oxygen analogs, and a series of their *para*-substituted benzaldehyde derivatives were synthesized. The dipole moments, infrared and ultraviolet spectra of some analogous carbamyl, thiocarbamyl and selenocarbamyl compounds were investigated. Evidence is cited that the contribution of the form with a separation of charge is greatest in the selenocarbonyl, less in the thiocarbonyl and least in the carbonyl group.

Since 1946, when Domagk[4] first reported the antitubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazone, large numbers of thiosemicarbazones were synthesized and tested.[5-7] Among these, highest antitubercular action was found to reside in a series of *para*-substituted benzaldehyde derivatives and somewhat lower but still considerable *in vitro* activity in thiosemicarbazide itself.[8] More recently it was found that thiosemicarbazide and thiosemicarbazones also possess some ability to inhibit the growth of fungi.[9,10]

Replacement of sulfur by oxygen resulted in complete or partial loss of both the antitubercular and the antifungal action of these compounds.[10,11]

Since it has been stated that thiosemicarbazones exert their antimicrobial action by forming copper chelates,[10,12,13] the lower effectiveness of semicar-

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(1) The material reported here represents part of a thesis submitted by Henry G. Mautner in partial fulfillment of the requirements for the Ph.D. degree in pharmaceutical chemistry.

(2) This paper was presented before the Division of Medicinal Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March–April, 1955.

(3) Fellow of the American Foundation for Pharmaceutical Education 1954–1955.

(4) G. Domagk, *et al.*, *Naturwissenschaften*, **33**, 315 (1946).

(5) R. Donovick, *et al.*, *J. Bact.*, **59**, 603 (1950).

(6) R. Donovick, *et al.*, *ibid.*, **59**, 667 (1950).

(7) E. Hoggarth, *et al.*, *Brit. J. Pharmacol.*, **4**, 248 (1949).

(8) J. P. Jouin and Buu-Hoi, *Ann. inst. Pasteur.*, **72**, 580 (1946).

(9) C. W. Johnson, J. W. Joyner and R. P. Perry, *Antibiotics & Chemotherapy*, **2**, 636 (1952).

(10) H. W. Gausman, *et al.*, *Botan. Gaz.*, **114**, 292 (1953).

(11) D. Hamre, J. Bernstein and R. Donovick, *J. Bact.*, **59**, 679 (1950).

(12) E. Carl and P. Marquardt, *Z. Naturforsch.*, **4B**, 280 (1949).

(13) K. Liebermeister, *ibid.*, **5B**, 79 (1950).

bazones as compared to thiosemicarbazones might be due to the lower tendency of the oxygen compounds to form such complexes.

In view of the fact that selenium is related to sulfur in the same way in which sulfur is related to oxygen, it was felt that selenosemicarbazides and their derivatives might possess still higher chelating and antimicrobial action than their sulfur analogs.

Preliminary attempts to prepare free selenosemicarbazide were not promising.[14]

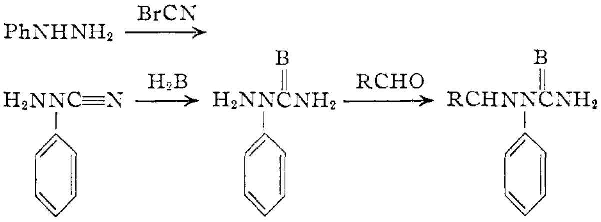
Attempts to add hydrogen selenide to N^{β}-cyanohydrazides to yield 1-acylselenosemicarbazides were unsuccessful. Subsequently, it was discovered that the "cyanohydrazides" were actually 5-substituted 1,2,4-Δ^4-triazolones.[15]

In view of the difficulties encountered in preparing selenosemicarbazide, it was decided to attempt to synthesize 2-phenylselenosemicarbazide, which, while substituted, has a free terminal nitrogen and could be used to form derivatives.

1-Cyano-1-phenylhydrazine was prepared by a modification of the method of Pellizzari.[16] Addition of the amine to cyanogen bromide rather than *vice versa*, increased the purity of the product, presumably since the avoidance of an excess of amine reduced the probability of forming diphenyldiaminoguanidine.

1-Cyano-1-phenylhydrazine was found to react smoothly with hydrogen selenide, 2-phenylselenosemicarbazide (III) being obtained in good yield. Addition of hydrogen sulfide gave 2-phenylthiosemicarbazide (II), previously obtained by a somewhat different method,[16] while treatment with hot potassium hydroxide resulted in the formation of 2-phenylsemicarbazide (I).[16]

I, II and III all reacted with aromatic aldehydes to form the respective semicarbazones, thiosemicarbazones and selenosemicarbazones.



where B is oxygen, sulfur or selenium

The selenium compounds proved to be quite stable if protected from direct light. Precipitation of colloidal selenium could be largely avoided by wrapping the reaction vessels in aluminum foil. The statement in the literature that it is impossible to perform routine combustion analyses of selenium compounds without fouling the train,[17] was not borne out. Carbon, hydrogen analyses were performed without difficulty.[18] The derivatives which were synthesized are shown in Table I.

In general, the crystal structures of selenosemicarbazones and their sulfur analogs appeared to be identical, but differed from that of their oxygen analogs.

Ultraviolet Spectra.—It has been known for some time that the wave lengths of maximum absorption of thiocarbonyl compounds are greater than those of corresponding carbonyl compounds.[19] In view of the inverse relationship between wave length, and the energy difference between the activated state and the ground state, this shift could be attributed either to labilization of the ground state (possibly due to the increased difficulty of forming a π-bond as interatomic distances are increased), or to stabilization of the activated state. In other words, the contribution of the form $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{S}}$ in the thiocarbonyl group would be greater than the contribution of the form $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{O}}$ in the carbonyl group, although on the basis of the electronegativities of oxygen and sulfur the opposite would be expected. It is possible that the stabilization of the activated form in the thiocarbonyl compounds might be attributed to the possibility of sulfur having more than eight orbitals available in which electrons could be accommodated. This idea had been postulated previously to account for the observation that a sulfur atom in the system $-\mathrm{S}-\overset{|}{\mathrm{C}}-\mathrm{H}$ has more proton-releasing effect on the adjoining carbon, than an oxygen atom in an analogous compound.[20–22]

It seemed important to determine whether in a series of analogous carbamyl, thiocarbamyl and selenocarbamyl compounds a further increase in the wave lengths of maximum absorption might be observed in passing from the sulfur to the selenium compounds. This was indeed found to be the case.

The colors of the *p*-nitrobenzaldehyde derivatives of I, II and III also changed in the expected fashion in descending the periodic table: the oxygen compound being faintly greenish-yellow ($\lambda_{\max}$ 334 mμ), the sulfur compound bright orange ($\lambda_{\max}$ 354 mμ), and the selenium compound bright red ($\lambda_{\max}$ 368 mμ).

It can, therefore, be assumed that the contribu-

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(14) The reaction of hydrazine sulfate with potassium selenocyanate did not yield the desired product, metallic selenium being precipitated. In analogy with the Wöhler synthesis of urea from ammonium cyanate, in which ammonia and cyanic acid rather than ammonium ion and cyanate ion have been cited as true reactants (see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 257) hydrazine and selenocyanic acid would be expected to be the reacting entities in the formation of selenosemicarbazide. It is possible that the failure of this reaction may be attributed to the extreme instability of free selenocyanic acid (see P. C. Thorne and E. R. Roberts, "F. Ephraim, Inorganic Chemistry," Fourth Ed., Interscience Publishers, Inc., New York, N. Y., 1943, p. 176). The reaction of hydrazine hydrate with ammonium selenocyanate also failed to give the desired product.

Selenosemicarbazide could not be prepared by the addition of hydrogen selenide to cyanohydrazine: the previously reported lack of stability of the latter compound (see H. Franzen and H. L. Lucking, *Z. anorg. Chem.*, **70**, 147 (1911) and E. Müller and L. Herrdegen, *J. prakt. Chem.*, **102**, 113 (1921)) was confirmed. Several other possible approaches to the synthesis of selenosemicarbazide were investigated without success (see H. G. Mautner, Ph.D. Thesis, University of California, 1955, pp. 8–11 and 19–24).

(15) H. G. Mautner and W. D. Kumler, THIS JOURNAL, **77**, 4076 (1955).

(16) G. Pellizzari, *Gazz. chim. ital.*, **37** [I], 611 (1907).

(17) T. W. Campbell, H. G. Walker and G. M. Coppinger, *Chem. Revs.*, **50**, 282 (1952).

(18) All analyses were carried out at the Microanalytical Laboratory of the Chemistry Department of the University of California.

(19) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 283 (1939).

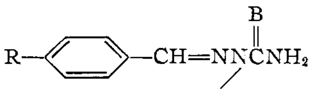
(20) E. Rothstein, *J. Chem. Soc.*, 1556 (1940).

(21) R. B. Woodward and R. H. Eastman, THIS JOURNAL, **68**, 2229 (1946).

(22) W. J. Brehm and T. Levenson, *ibid.*, **76**, 5389 (1954).

TABLE I

SEMICARBAZONES, THIOSEMICARBAZONES
SELENOSEMICARBAZONES



B = O, S, Se

Compd.	R	M.p., °C.[a,b]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
			(I) Semicarbazones				
1	Nitro	221.0–222.0	$C_{14}H_{12}O_3N_4$	59.15	58.94	4.25	4.26
2	Chloro	186.0–187.0	$C_{14}H_{12}ON_3Cl$	61.43	61.33	4.42	4.65
			(II) Thiosemicarbazones				
3	Nitro	223.0–224.0	$C_{14}H_{12}O_2N_4S$	55.99	55.72	4.03	4.04
4	Chloro	200.0–200.5	$C_{14}H_{12}N_3SCl$	58.03	58.20	4.18	4.20
5	Bromo	196.5–197.6	$C_{14}H_{12}N_3SBr$	50.30	50.47	3.62	3.77
6	Iodo	191.0–191.5	$C_{14}H_{12}N_3SI$	44.10	44.29	3.17	3.09
			(III) Selenosemicarbazones				
7	...	178.0–179.0	$C_{14}H_{13}N_3Se$	55.63	55.72	4.34	4.22
8	Nitro	213.0–214.0	$C_{14}H_{12}O_2N_4Se$	48.43	48.70	3.48	3.73
9	Chloro	196.0–198.0	$C_{14}H_{12}N_3SeCl$	49.94	50.14	3.59	3.82
10	Bromo	190.5–191.5	$C_{14}H_{12}N_3SeBr$	44.12	44.20	3.17	3.30
11	Iodo	184.5–185.0	$C_{14}H_{12}N_3SeI$	39.27	39.41	2.83	2.93
12	$(CH_3)_2N-$	158.5–159.5	$C_{16}H_{18}N_4Se$	55.65	55.83	5.26	5.31
13	Acetamido	194.5–195.0	$C_{16}H_{16}ON_4Se$	53.48	53.82	4.49	4.69
14	Methoxy	178.0–179.0	$C_{15}H_{15}ON_3Se$	54.22	54.53	4.55	4.70
15	Hydroxy	175.0–176.0	$C_{14}H_{13}ON_3Se$	52.84	52.84	4.12	4.23

[a] All m.p.'s are corrected. [b] The m.p.'s of the selenium compounds generally depended somewhat on the rate of heating and the temperature at which the samples were added.

TABLE II

Compound	λmax, mμ	εmax	Bands in NH region, μ		
Urea			3.06	2.99	2.89
Thiourea			3.15	3.05	2.95
Selenourea			3.17	3.06	2.98
Phenylurea	238	15,600	3.10	3.02	2.90
Phenylthiourea	267	10,950	3.13	3.04	2.90
Phenylselenourea	275	11,450	3.15	3.05	2.92
2-Phenylsemicarbazide (I)	242	10,050	3.13	3.06	2.87
2-Phenylthiosemicarbazide (II)	255	8,200	3.19	3.08	2.91
2-Phenylselenosemicarbazide (III)	271	7,280	3.19	3.09	2.91

tion of the form $-\overset{+}{N}H=\overset{\overset{B^-}{|}}{C}-NH_2$ (B = O, S, Se) increased in passing from analogous ureides to thioureides to selenoureides.

Infrared Spectra.—It seemed likely that as the polarized forms $-\overset{+}{N}H=\overset{\overset{B^-}{|}}{C}-NH_2$ (B = O, S, Se) increased in importance, the -NH groups should show increasing evidence of being associated. In view of the well-established fact that the wave lengths resulting from -NH stretching vibrations are increased by hydrogen bonding,[23,24] it was undertaken to investigate the infrared spectra of three series of analogous carbamyl, thiocarbamyl and selenocarbamyl compounds. In each series the expected frequency changes were observed.

Dipole Moments.—On the basis of the electronegativities of oxygen, sulfur and selenium, one would expect[25] that in analogous carbamyl, thiocarbamyl and selenocarbamyl compounds the dipole moments should progressively decrease from the oxygen to the selenium compounds.

If, however, the contribution of the form $-\overset{+}{N}H=\overset{\overset{B^-}{|}}{C}-NH_2$ (B = O, S, Se) increases in the opposite direction, as shown by spectroscopic data, the selenium compounds should have greater dipole moments than their sulfur analogs, which in turn should have greater dipole moments than the oxygen compounds.

The dipole moments of phenylurea, phenylthiourea, phenylselenourea, I, II, III, semicarbazide and thiosemicarbazide were measured. The moments were determined in dioxane at 30°, that of II also being measured in benzene at 30°. Calculations were made by means of the Halverstadt–Kumler equation.[26] The plots of ϵ_{12} *vs.* ω_2, and of ν_{12} *vs.* ω_2 were found to be straight lines within the limits of experimental error. The solute molar electronic polarization P_{E_2} was measured for all the compounds investigated, except where otherwise indicated.

Results are summarized in Table III. It can be seen that in every case dipole moments increased from the oxygen to the sulfur to the selenium compounds.

A re-examination of the dipole moment of phenylurea, which previously had been reported as

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(23) F. A. Miller in H. Gilman, "Organic Chemistry, an Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 123.

(24) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 215.

(25) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 68.

(26) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

TABLE III

EMPIRICAL CONSTANTS, POLARIZATIONS, REFRACTIONS AND DIPOLE MOMENTS

Compound	ϵ_1	v_1	n_1^2	α	β	γ	P_{20}	P_{E20}	μ
Phenylurea	2.2108	0.97786	2.00972	18.8	−0.363	0.60	447.56	35.99	4.525
Phenylthiourea	2.2121	.97816	2.01001	21.5	− .245	.68	573.40	46.98	5.12
Phenylselenourea	2.2118	.97823	.....	19.0	− .532	.66	651.42	48.76[a]	5.49
I	2.2172	.97819	2.00957	14.0	− .275	.505	379.88	40.70	4.11
II	2.2157	.97806	2.00961	19.9	− .263	.69	584.50	51.19	5.15
II (benz.)	2.2797	1.15149	.....	15.3	− .820	.80	477.72	51.19[b]	4.67
III	2.2163	0.97804	2.00982	18.2	− .38	.54	680.15	53.35	5.58
Semicarbazide	2.2174	.97803	.....	24.0	− .66	.235	304.12	18.99[c]	3.77
Thiosemicarbazide	2.2162	.97801	2.00974	39.1	− .365	.77	604.29	26.87	5.36

[a] The P_{E20} was calculated, assuming a value of 13.1 for the C=Se group. [b] Used value obtained in dioxane. [c] Calculated.

3.6 D[27] yielded a value of 4.52 D. This is very close to the dipole moment of urea, which was found to be 4.56 D.[28] It appears, therefore, that the phenyl group plays a less important role in reducing the moment of urea than had been postulated previously.[28]

It should be noted that the increase in dipole moment in moving from thiocarbamyl to selenocarbamyl compounds is too large in comparison to the increase in dipole moment from the carbamyl to the thiocarbamyl compounds, to be attributed to the increase of covalent radius as oxygen is replaced by sulfur and selenium (=O, 0.55 Å.; =S, 0.94 Å.; =Se, 1.07 Å.[29]).

Since the increase in wave length of maximum absorption in passing from analogous oxygen to sulfur to selenium compounds is associated, as previously discussed, with a greater contribution of the forms with a separation of charge $-\overset{+}{N}H=\overset{\overset{B^-}{|}}{C}-NH_2$ which would result in increased dipole moments, it might be expected that μ would increase in the same way as does λ_{max}.

It can be seen (Fig. 1) that in both the phenylurea, and the phenylsemicarbazide series, plotting dipole moment *vs.* wave lengths of maximum absorption did indeed result in good approximations to straight line relationships.

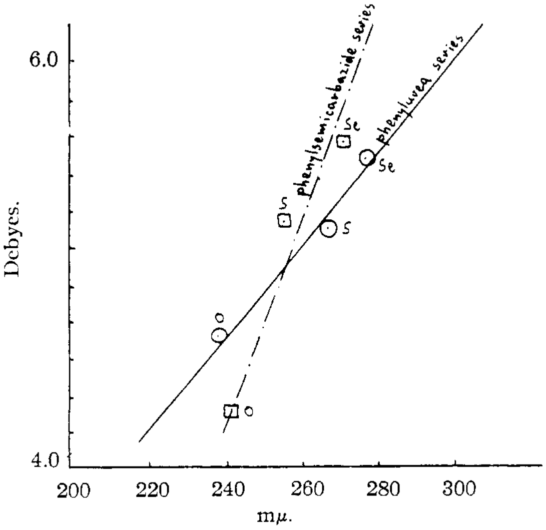
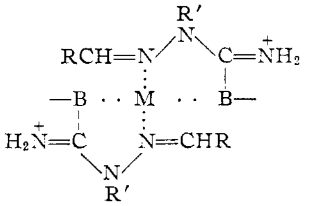


Fig. 1.—Plot of dipole moments *vs.* wave lengths of maximum absorption.

Discussion

The measurements cited lead to the conclusion that the importance of charge-separated resonance forms increases as the oxygen in carbamyl compounds is successively replaced by sulfur and selenium.

It seems possible that this observation might be related to the higher ability of sulfur than of oxygen compounds to form chelates. It seems likely that the formation of a complex would be favored by



M = metal
B = O, S, Se

increasing the basicity of B which, because of the resonance cited above, should progressively rise from oxygen to sulfur to selenium.

Since the antimicrobial activity of thiosemicarbazones has been stated as being related to their ability to chelate copper,[10,12,13] the antifungal[30] and antitubercular activities of the compounds synthesized in this study were investigated. The selenium compounds were found to be between ten to one thousand times more effective on a molar basis than their sulfur analogs, while the oxygen compounds generally showed only slight activity.

Experimental

Materials. 1-Cyano-1-phenylhydrazine.—A modification of the method of Pellizzari[20] was used. A solution of 163 g. (1.535 moles) of cyanogen bromide in 1 l. of ethanol was poured into 5 l. of water in a 12-l. round-bottom flask equipped with an efficient stirrer. With agitation 151 cc. (1.535 moles) of freshly redistilled phenylhydrazine was added in small portions. Stirring was continued at room temperature for 1.5 hours. Filtration yielded 44.0 g. of faintly cream-colored crystals. Extraction of the filtrate with four 200-cc. portions of ether and working up of the ether extracts yielded more product to bring the total yield to 33.3%. The 1-cyano-1-phenylhydrazine was recrystallized from ethanol; m.p. 88.0–89.0°, lit.[20] m.p. 89°.

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(27) G. Devoto and R. Di Nola, *Gazz. chim. ital.*, **63**, 495 (1933).

(28) W. D. Kumler and G. M. Fohlen, THIS JOURNAL, **64**, 1944 (1942).

(29) L. Pauling, "The Nature of the Chemical Bond," Sec. Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 164.

(30) H. G. Mautner, W. D. Kumler, Y. Okano and R. Pratt, accepted for publication in *Antibiotics and Chemotherapy*.

2-Phenylsemicarbazide (I).—1-Phenyl-1-cyanohydrazine was treated with boiling aqueous 10% potassium hydroxide.[20] On cooling the product separated in the form of coarse needles. The orange filtrate was extracted with chloroform, from which more 2-phenylsemicarbazide could be isolated to raise the total yield to 82%. The product was recrystallized from chloroform; m.p. 119.5–120.5°, lit.[20] m.p. 118–119°. The sample used for dipole moment measurements was recrystallized three times.

2-Phenylthiosemicarbazide (II).—A solution of 4.0 g. (0.03 mole) of 1-cyano-1-phenylhydrazine and 2.5 cc. of concentrated ammonium hydroxide in 28 cc. of ethyl alcohol was heated to 50°, while hydrogen sulfide was bubbled through the mixture for 2.5 hours. On cooling, 4.0 g. of white needles, representing a yield of 79.6%, separated. The sample used for dipole moment work was recrystallized three times from 50% ethanol.

2-Phenylselenosemicarbazide (III).—A solution of 3.0 g. (0.0226 mole) of 1-phenyl-1-cyanohydrazine in a mixture of 24 cc. of ethanol and 2.1 cc. of concentrated ammonium hydroxide was heated to 60°. Hydrogen selenide freshly prepared by treating aluminum selenide[31] with dilute acid was bubbled through the mixture for 3.5 hours. After cooling the coarse, gray crystals were filtered off, washed with water, dried and recrystallized from absolute ethyl alcohol. A yield of 3.5 to 4.5 g. (72 to 93%) of delicate, white needles melting at 166.0–166.5° dec. was obtained.

Anal. Calcd. for $C_7H_9N_3Se$: C, 39.26; H, 4.24; N, 19.64. Found: C, 39.48; H, 4.21; N, 19.91.

The sample used for dipole moment measurements was recrystallized three times.

Derivatives of I, II and III.—Compounds I, II or III were refluxed for 24 hours with a slight excess of aldehyde in ethanol or methanol to which a few drops of acetic acid had been added. The semicarbazones, thiosemicarbazones or selenosemicarbazones obtained on cooling were recrystallized from ethanol or methanol.

The *p*-iodobenzaldehyde derivatives (compds. 6 and 11) separated as voluminous masses of fibrous needles, which on standing in solution changed to chunky prisms, possibly indicating *cis–trans* isomerism. Compound 15 was found to form an addition complex with benzene.

Treatment of I, II and III with Cupric Sulfate.—In flasks containing 10 cc. of methanol each, were dissolved 0.0001-mole samples of I, II and III, respectively. To each of the colorless solutions was added 0.100 g. (0.0004 mole) of cupric sulfate in 10 cc. of methanol. The following colors were observed: I, unchanged; II, clear turquoise green; III, dark olive-green rapidly lightening to grass green. A greenish-yellow flocculent precipitate soon separated from the solution containing III, the other solutions remaining clear after 12 hours.

Selenourea.—The method of Verneuil[32] involving the addition of hydrogen selenide twice to cyanide was utilized. The product was recrystallized twice from absolute ethanol; m.p. 210.0–211.0° dec., m.p. lit.[33] 200°.

Phenylselenourea.—Hydrogen selenide was added to freshly prepared phenyl cyanamide according to the procedure of Zingaro.[33] The dipole moment sample was recrystallized three times from absolute ethanol.

Semicarbazide.—Hydrazine sulfate was permitted to react with potassium cyanate.[34] The product was recrystallized three times from absolute ethanol.

Thiosemicarbazide, Phenylurea, Phenylthiourea.—Commercial, best quality products were recrystallized three times from 50% ethanol.

Ultraviolet Spectra.—A Cary recording spectrophotometer model 11 PMS with quartz cells was utilized. Solutions were made up in volumetric flasks with absolute ethanol from weighed quantities of the compounds.

Infrared Spectra.—Measurements were made with a Perkin–Elmer model 21 infrared spectrophotometer, using perfluorokerosene mulls.

Dipole Moments.—The heterodyne-beat method was used. Solvents were purified as previously indicated.[35]

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

A Cleavage of Certain α,β-Unsaturated Ketones by Alkaline Hydrogen Peroxide

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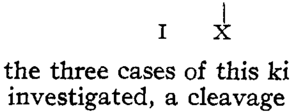
The α′-substituted α,β-unsaturated ketones N-acetyl-1-*p*-chloroanilino-4-phenyl-3-butene-2-one (II) and N-acetyl-1-anilino-1,4-diphenyl-3-butene-2-one (IV) were not converted into the corresponding epoxides by alkaline hydrogen peroxide in aqueous ethanol but underwent oxidative cleavage instead. Compound II yielded *p*-chloroacetanilide and compound IV yielded benzanilide; other identified products from the reaction with IV were benzaldehyde and acetaldehyde. The hypothesis that this type of cleavage is characteristic of α,β-unsaturated ketones with functional groups in the α′-position led to the finding that cinnamoyldibenzoylmethane (VIII) is cleaved in an apparently similar manner. A partial explanation of these cleavage reactions is suggested.

Oxidation with alkaline hydrogen peroxide, as described by Weitz and Scheffer[3] in 1921, has been used successfully for preparation of the epoxides of many α,β-unsaturated ketones and aldehydes. We wish to report, however, that alkaline hydrogen peroxide oxidation can follow quite a different course in the case of α,β-unsaturated ketones of the type I, wherein certain functional groups X and one or two hydrogen atoms are present in the α′-position. In the three cases of this kind which we have thus far investigated, a cleavage of the molecule into three or more fragments has occurred.



$$C_6H_5CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}{-}R$$

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[2] Research Corporation Fellow, 1951–1952. This paper is based mainly on a portion of a thesis submitted by David I. Sapper in partial fulfillment of the requirements for the degree of Doctor of Science at the Carnegie Institute of Technology, July, 1952.

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