(4) J. P. Freeman and J. J. Cannon, *J. Heterocycl. Chem.*, **3**, 544 (1966).
(5) J. P. Freeman and J. J. Cannon, *J. Org. Chem.*, **34**, 194 (1969).
(6) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).
(7) A. McKillop and R. J. Kobylecki, *Tetrahedron*, **30**, 1365 (1974).
(8) F. R. Stermitz and D. W. Neiswander, *Tetrahedron*, **31**, 655 (1975); F. R. Stermitz and F. A. Norris, *J. Org. Chem.*, **35**, 527 (1970).
(9) M. C. Aversa, G. Cum, and M. Crisafulli, *Gazz. Chim. Ital.*, **98**, 42 (1968).
(10) A. Quilico and P. Grünanger, *Gazz. Chim. Ital.*, **85**, 1449 (1955).
(11) A. Quilico, G. Stagno d'Alcontres, and P. Grünanger, *Nature (London)*, **166**, 226 (1950).
(12) G. Stagno d'Alcontres and P. Grünanger, *Gazz. Chim. Ital.*, **80**, 741 (1950).
(13) R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, **100**, 1802 (1967).
(14) R. G. Micetick, *Can. J. Chem.*, **48**, 467 (1970).
(15) L. B. Clapp, *J. Chem. Educ.*, **20**, 189 (1943).
(16) T. H. Liu and K. Toriyama, *Can. J. Chem.*, **50**, 3009 (1972).
(17) A. Quilico and P. Grünanger, *Gazz. Chim. Ital*, **85**, 1250 (1955).
(18) This experiment was taken from the M.S. Thesis of Miss Nazir Anjum, Punjab University, Lahore, Pakistan, 1975.
(19) E. ter Meer, *Justus Liebigs Ann. Chem.*, **181**, 4 (1876); L. F. Fieser and W. von E. Doering, *J. Am. Chem. Soc.*, **68**, 2252 (1946).

Iodonium Ylides. Reactions of Phenyldimedonyliodone with Several Thiocarbonyl Compounds. Evidence for Sulfur Ylide Intermediates

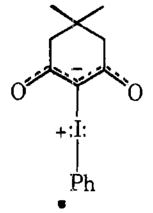
Gerald F. Koser* and Shwn-Meei Yu

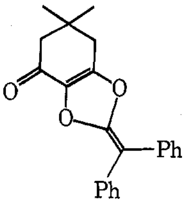
Department of Chemistry, The University of Akron, Akron, Ohio 44325

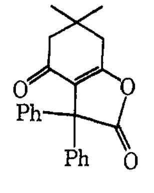
Received July 14, 1975

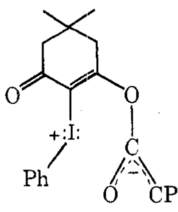
When phenyldimedonyliodone (1) was allowed to react with phenyl isothiocyanate, the products were iodobenzene, 7 (8%), 8 (36%), and 9 (14%). Similar reaction of 1 with methyl isothiocyanate gave 7 (35%) and 9 (26%). The intermediacy of sulfur ylide 11, an analogous sulfur ylide from 1 and methyl isothiocyanate, and thiotrione 12 in those reactions seems to be indicated. An attempt to synthesize authentic 12 by treatment of 1 with hydrogen sulfide failed. However, compound 9 was isolated in 40% yield. Finally, when 1 was allowed to react with thiourea, the delocalized sulfur ylide 13 was obtained (67%).

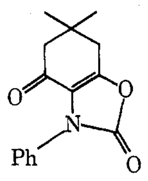
The formation of halonium ylides as reactive intermediates when certain carbenes are generated in the presence of organic halides is now a matter of record.[1-7] However, because of their instability, the halonium ylides have largely eluded isolation and study. Partially for that reason, we began an investigation of the chemical properties of phenyldimedonyliodone (1), a stable iodonium ylide which can be prepared by the condensation of dimedone with iodosobenzene diacetate.[8] Our first objective was to characterize the reactivity of 1 toward several electrophilic heterocumulenes, and we have already reported that 1 reacts with diphenylketene to afford ketene acetal 2 and lactone 3, presumably through the betaine 4, while phenyl isocyanate reacts with 1 to afford azalactone 5.[9] We now wish to report that the reaction of 1 with phenyl isothiocyanate takes a markedly different course, and, while we fully expected to obtain adduct 6, that compound was not isolated. In connection with this, the reactions of 1 with methyl isothiocyanate, hydrogen sulfide, and thiourea were also studied.

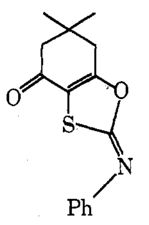

1


2


3

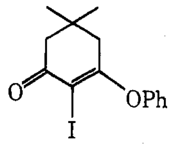

4

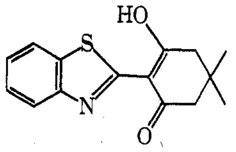

5

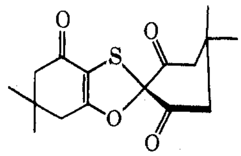

6

Results and Discussion

When phenyldimedonyliodone (1) and phenyl isothiocyanate were allowed to react in dichloromethane at room temperature, three products were obtained. One of these, isolated in 8% yield, was identified as phenyl 2-iododimedonyl ether (7), a known rearrangement product.[10] A second compound, isolated in 36% yield, was 2-(2-benzthiazolyl)dimedone (8), the structure of which was confirmed by its comparison with authentic material prepared by the action of bromine on dimedone-2-thiocarboxanilide (10).[11]


7


8


9

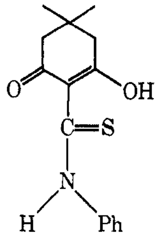
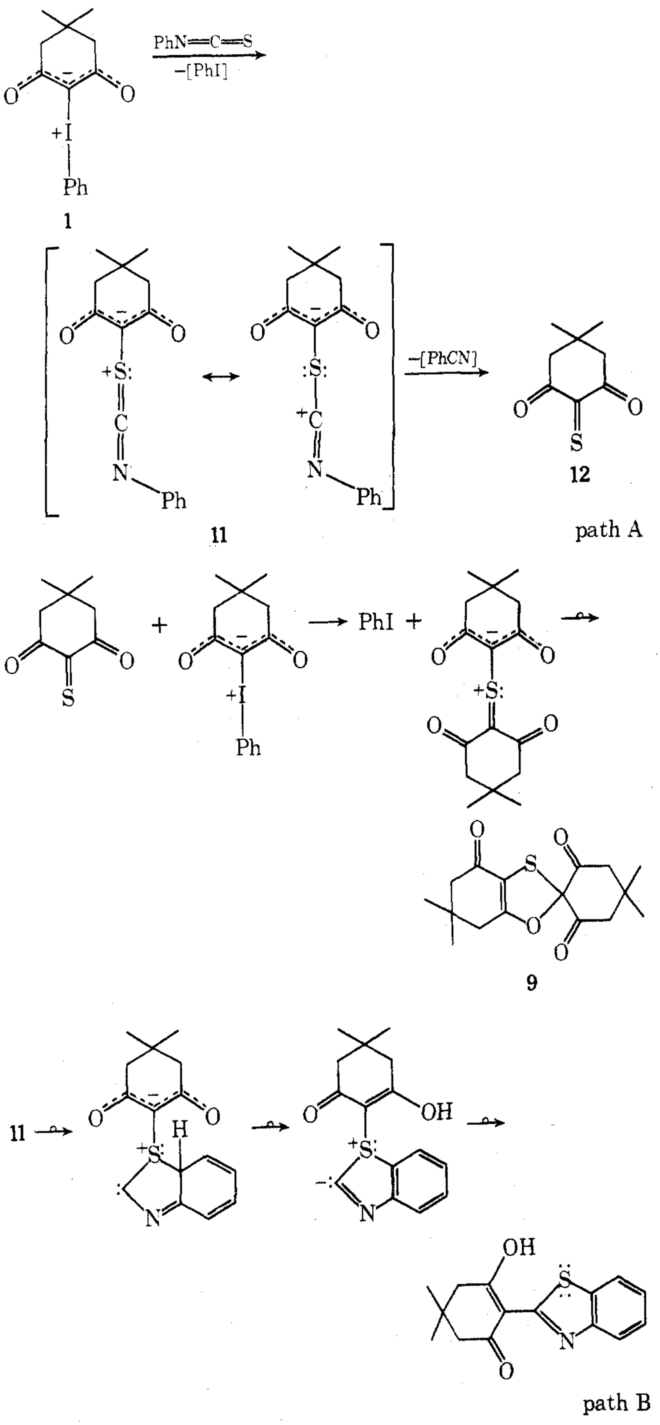

10

Chart I



The third product, a yellow solid isolated in 14% yield, was identified as **9** by elemental and spectral analysis. In particular, the 300-MHz ^{1}H NMR spectrum of **9** clearly reveals two "types" of dimedone rings, one with enol symmetry and one with keto symmetry. The former exhibits a six-proton singlet at δ 1.16 and a pair of two-proton singlets at δ 2.31 and 2.60 while the latter shows a pair of three-proton singlets at δ 0.89 and 1.23 and a pair of two-proton doublets at δ 2.51 and 3.01 ($J_{\text{gem}} \cong 13.5$ Hz). Iodobenzene is also formed in this reaction, and, in a separate study, the yield of iodobenzene was determined by GLC analysis to be 86%.

Several plausible reaction pathways for the formation of iodobenzene, **8**, and **9** from **1** and phenyl isothiocyanate are illustrated in Chart I.

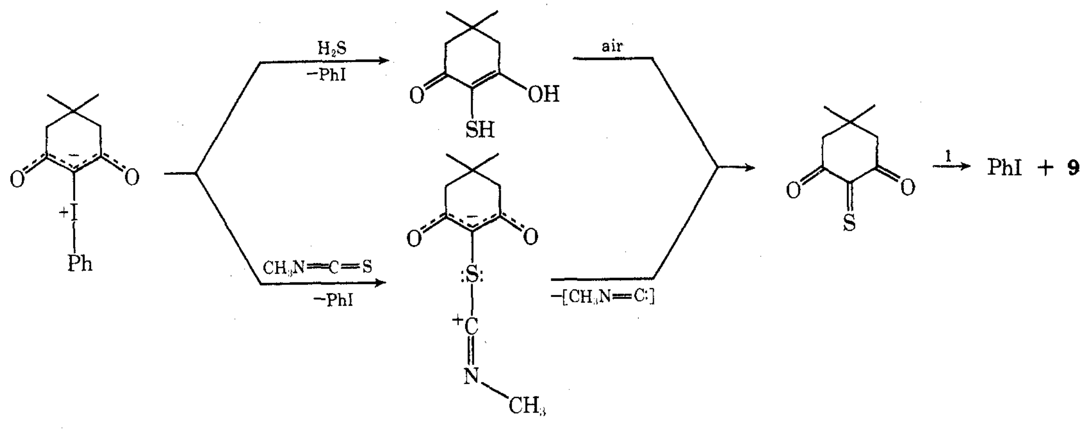
In this scheme, reaction is presumed to be initiated by displacement of iodobenzene from **1** by phenyl isothiocyanate with formation of sulfur ylide **11** which could then react in one of two ways. It could undergo an intramolecular rearrangement which eventuates in thiazole **8** (path B) or it could fragment to phenyl isocyanide and thiotrione **12** (path A). Subsequent attack of **12** on **1** would yield **9**. The proposed sulfur ylide **11** possesses several features which should drive the indicated rearrangement; it has a nucleophilic sulfur atom, positive charge which is most certainly delocalized into the benzene ring, and a basic oxygen atom situated favorably for deprotonation of the benzene ring at the right moment. Evidence bearing on this sequence of events was provided by the following experiments.

Phenyl isocyanide has not been isolated from the reaction of **1** with phenyl isothiocyanate. However, an insoluble, high melting (~290°) white solid was isolated. The solid exhibits no distinctive spectral features, but it does contain 5.1% nitrogen and only trace amounts of sulfur.

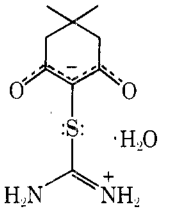
An attempt to synthesize **12** by treatment of **1** with hydrogen sulfide was unsuccessful. However, compound **9** was isolated in 40% yield. Also, when **1** was allowed to react with methyl isothiocyanate, the products were **7** (36%) and **9** (26%). It seems likely that both reactions proceed through a common intermediate, and one which is independent of the structural diversity of hydrogen sulfide and methyl isothiocyanate, and it seems plausible that **12** is that intermediate (Chart II).

Finally, we sought corroborative evidence that compounds containing the $>C{=}\ddot{S}{:}$ moiety can indeed displace iodobenzene from **1**. To this end, phenyldimedonyliodone was allowed to react with thiourea at room temperature, and compound **13** was isolated in 67% yield as a white, crystalline solid. The cyclic structure **14** for the white solid is clearly inconsistent with its NMR spectrum. Specifically, the methylene groups give rise to a four-proton singlet rather than a pair of two-proton singlets as expected for

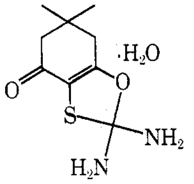
Chart II



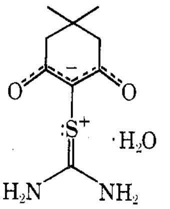
that structure. Also, we regard **13** as a more accurate representation of the true structure than **15** because the infrared spectrum of the white solid exhibits an absorption band at 1645 cm^{-1} ($-C{=}N^+H_2$ stretch). Thus, the known sulfonium ylide **16**[12] does not absorb in that region, but methylthiouronium bisulfate (**17**) does.[13]



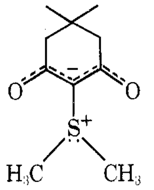
13



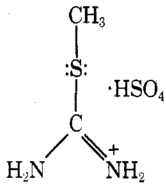
14



15



16



17

The formation of **13** from phenyldimedonyliodone and thiourea provides excellent analogy for the proposed formation of **9** from phenyldimedonyliodone and thiotrione **12**. However, in the case of **9**, the cyclic structure is favored over the dipolar structure, presumably because the carbonyl groups of the thiotrione moiety would inhibit the delocalization of positive charge.

Experimental Section

General. ^1H NMR spectra (60 MHz) were recorded on a Varian Model A-60 NMR spectrometer (relative to internal Me_4Si), infrared spectra on a Perkin-Elmer Model 337 spectrophotometer, and ultraviolet spectra on a Cary-17 uv-visible-ir spectrophotometer. ^1H NMR spectra (300 MHz) were recorded on a Varian Model HR-300 NMR spectrometer at The University of Akron's NMR center. Melting points are uncorrected. GLC analyses were conducted on a Hewlett-Packard Model 5750 gas chromatograph, a 6 ft column of 10% Ucon W-98 on 80–100 mesh silica being utilized. Elemental compositions were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reaction of Phenyldimedonyliodone (1) with Phenyl Isothiocyanate. A solution of **1** (10.98 g, 32.09 mmol) in CH_2Cl_2 (50 ml) and a solution of phenyl isothiocyanate (6.24 g, 46.16 mmol) in CH_2Cl_2 (50 ml) were mixed and allowed to stir for 4.5 days at room temperature. The CH_2Cl_2 was then evaporated in vacuo, and the brown, viscous liquid which remained was resolved by column chromatography on Florisil (250 g). Twenty-one fractions of ca. 300 ml each were collected as the elution solvent was changed in a systematic way: 1 (C_6H_{12}), 2–3 (C_6H_{12}–ether, 50:50), 4 (C_6H_{12}–ether, 20:80), 5–8 (ether), 9 (ether–$CH_3CO_2C_2H_5$, 80:20), 10 (ether–$CH_3CO_2C_2H_5$, 50:50), 11 (ether–$CH_3CO_2C_2H_5$, 20:80), 12–13 ($CH_3CO_2C_2H_5$), 14 ($CH_3CO_2C_2H_5$–CH_2Cl_2, 50:50), 15–16 (CH_2Cl_2), 17 (CH_2Cl_2–CH_3OH, 50:50), 18–21 (CH_3OH). Each fraction was then concentrated and subjected to NMR analysis. Fractions 5–9 gave 1.71 g of reasonably pure **8**, but further resolution of other fractions was necessary before pure materials could be isolated.

Fractions 2 and 3. The crude solid (1.31 g) was divided by hand into colorless crystals (**7**) and yellow crystals (**9**). The yellow material (0.70 g) was chromatographed on Florisil (50 g), six fractions of ca. 300 ml each being collected. The first four fractions (benzene) yielded 0.41 g of **9** while the last two fractions (ether) yielded 0.24 g of **7**.

Fraction 4. The crude solid (0.59 g) was rechromatographed on Florisil (50 g), six fractions of about 300 ml each being collected. The first fraction (benzene) gave nothing, the second fraction (benzene–ether, 90:10) gave 0.23 g of mostly **7**, the third fraction (benzene–ether, 90:10) gave 0.05 g of mostly **7**, and the fourth fraction (ether) gave 0.18 g of **8**.

Fractions 14–17. The crude solids (5.29 g) were combined and triturated with cyclohexane–ether (50:50), and 4.37 g of phenyldimedonyliodone was recovered as a white powder. The washings were concentrated and yielded 0.9 g of a thick, brown liquid which has not been identified.

Fraction 18. This solid–liquid (1.05 g) was washed with ether and combined with the solids (1.24 g) from fractions 19–21. In this way, 2.12 g of a high melting (~290°), highly insoluble, yellow solid was obtained.

Anal. Found: C, 64.29; H, 5.77; N, 5.07; S, 0.28.

The product yields based on the amount of unrecovered **1** (19.317 mmol) follow: **7** (0.52 g, 7.8%), **8** (1.89 g, 35.8%), and **9** (0.41 g, 13.8%).

Purification and Characterization of 8. The crude material was recrystallized from dichloromethane–cyclohexane as white plates: mp 200–201°; uv (CH_2Cl_2) 259 nm (max, ϵ 14179, conjugated benzene ring), 239 (sh, 10672), 271 (sh, 9925), 347 (max, 35149), 334 (sh, 26716); uv (CH_3OH) 260 nm (max, ϵ 13750), 238 (sh, 8945), 271 (sh, 10078), 344 (max, 33164), 331 (sh, 26406), 314 (sh, 11797); ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (s, 6 H), 2.49 (s, 2 H), 2.54 (s, 2 H), 7.38 (t, 1 H), 7.52 (t, 1 H), 7.60 (d, 1 H), 7.83 (d, 1 H), 16.5 (s, 1 H); ^1NMR (60 MHz, $CDCl_3$) δ 1.12 (s, 6 H), 2.53 (s, 4 H), sometimes is recorded as a moderately resolved pair of singlets, 7.2–8.0 (complex m, 4 H), 16.5 (broad s, exchanges with D_2O).

Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; S, 11.73. Found: C, 65.98; H, 5.63; S, 11.55.

Purification and Characterization of 9. The crude material was recrystallized from dichloromethane–cyclohexane as yellow needles: mp 176–178°; ir (KBr) 5.84 (C=O, saturated ketone), 6.04 (C=O, α,β-unsaturated ketone), 6.20 μ (C=C); uv-visible (CH_3OH) 306 nm (max, ϵ 4175), 289 (sh, 3744), 380 (tail, 150); uv-visible (CH_2Cl_2) 292 nm (max, ϵ 4610) 312 (sh, 4082), 380 (tail, 120), 246 (plateau, 1774); ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, 3 H), 1.16 (s, 6 H), 1.23 (s, 3 H), 2.31 (s, 2 H), 2.51 (d, 2 H, $J_{gem} \cong$ 13.5 Hz), 2.60 (s, 2 H), 3.01 (d, 2 H, $J_{gem} \simeq$ 13.5 Hz); ^1H NMR (60 MHz, $CDCl_3$) δ 0.88 (s, 3 H), 1.15 (s, 6 H), 1.23 (s, 3 H), 2.30 (s, 2 H), 2.33 (shoulder, 0.5 H), 2.58 (apparent s, 3.5 H), 2.94 (broad apparent s, 1.5 H), 3.18 (broad apparent s, 0.5 H).

Anal. Calcd for $C_{16}H_{20}SO_4$: C, 62.31; H, 6.54; S, 10.40. Found: C, 62.51; H, 6.72; S, 10.74.

Reaction of 1 with Phenyl Isothiocyanate. Yield of Iodobenzene. A solution of **1** (3.0520 g, 8.919 mmol) in CH_2Cl_2 (20 ml) and a solution of phenyl isothiocyanate (1.9510 g, 14.432 mmol) in CH_2Cl_2 (20 ml) were mixed and allowed to stir for 5 days at room temperature. The reaction mixture was then diluted volumetrically to 50 ml with CH_2Cl_2. A 10-ml aliquot was removed, 0.1073 g (0.799 mmol) of durene was added, and the resulting solution was subjected to GLC analysis. Two separate injections yielded an average iodobenzene–durene peak area ratio of 1.247. A known mixture of durene (0.1900 g, 1.416 mmol) and iodobenzene (0.4061 g, 1.991 mmol), when subjected to similar analysis, gave an iodobenzene–durene peak area ratio of 0.917. Thus, the iodobenzene–durene peak area ratio must be multiplied by a factor of 1.533 to give the correct iodobenzene–durene mole ratio. The yield of iodobenzene was, therefore, 85.7%.

The 10-ml GC sample was then combined with the remaining 40 ml of solution, the CH_2Cl_2 was evaporated in vacuo, and the residue was resolved by column chromatography on Florisil. Seven fractions of about 300 ml each were collected and concentrated, and the residues were subjected to NMR analysis. Fractions 1–3 (ether) yielded a mixture of **7**, **8**, and **9** and fractions 4–5 ($CH_3CO_2C_2H_5$) gave 0.71 g of mostly unreacted **1**.

The crude solids from fractions 4 and 5 were combined and washed with ether, and 0.3217 g (0.940 mmol) of **1** was recovered as a white powder. The iodobenzene yield, based on the amount of unrecovered **1**, was 95.76%.

Reaction of Phenyldimedonyliodone (1) with Methyl Isothiocyanate. A solution of **1** (9.156 g, 26.76 mmol) in CH_2Cl_2 (50 ml) and a solution of methyl isothiocyanate (2.46 g, 33.64 mmol) in CH_2Cl_2 (50 ml) were mixed and allowed to stir under nitrogen for 5 days at room temperature. The solvent was then evaporated in vacuo, and the crude product was resolved by column chromatography on Florisil. Nine fractions of ca. 300 ml each were collected, concentrated, and subjected to NMR analysis. The details are given in Table I.

Fraction 2 was resolved into its components by a second chromatography on Florisil with cyclohexane followed by benzene followed by ether as the elution solvents. In this way, 0.160 g of **7** and 0.390 g of **9** was obtained.

Fraction 9 was triturated with ether and 5.873 g of unreacted **1** was recovered.

Table I

Fraction	Solvent	Wt, g	State	Identification
1	Benzene	0.156	Liquid	**7** + C_6H_5I
2	Benzene–ether (90:10)	0.570	Solid	**7** + **9** (~1:3)
3	Benzene–ether (50:50)	0.699	Solid	Mostly **7**
4	Ether	0.233	Solid	Mostly **7**
5	Ether	0.065	Solid	Mostly **7**
6	Ether	0.016	Solid	**7** + unknown
7	$CH_3CO_2C_2H_5$	0.031	Solid	**7** + unknown
8	CH_2Cl_2	0.221	Solid	**1** + unknown
9	CH_2Cl_2–CH_3OH (50:50)	6.468	Solid	Mostly **1**

Hence, the yields of **7** and **9**, based on the amount of **1** which had reacted (9.594 mmol), were 35 and 26%.

Reaction of Phenyldimedonyliodone (1) with H_2S. A solution of **1** (10.01 g, 29.25 mmol) in CH_2Cl_2 (120 ml) was saturated with H_2S for 30 min and allowed to stir overnight at room temperature. The solvent was then removed by vacuum evaporation, and the crude yellow-white solid which remained was resolved by column chromatography on Florisil (200 g). Twenty fractions of ca. 300 ml each were collected as the elution solvent was changed in a systematic way: 1 (C_6H_{12}), 2–7 (C_6H_{12}–ether, 90:10), 8–12 (C_6H_{12}–ether, 85:15), 13–14 (C_6H_{12}–ether, 80:20), 15 (C_6H_{12}–ether, 50:50), 16 (ether), 17 (ether-$CH_3CO_2C_2H_5$, 50:50), 18 ($CH_3CO_2C_2H_5$), 19–20 (CH_3OH). Each fraction was then concentrated, and some of them were subjected to NMR analysis. Fractions 4–13 yielded 1.4247 g of relatively pure **9**, fractions 2–3 gave 0.3019 g of mostly **9** (contaminated with some iodobenzene), and fractions 14–18 gave 0.7126 g of mostly unknown material contaminated with **9**. A second chromatography of that material yielded 0.0830 g of **9**. Thus, the total yield of **9** was ~1.8096 g (40%).

Authentic 2-(2-Benzthiazolyl)dimedone (8). This material was prepared by the method of Barnikow.[11] In the first step, dimedone was condensed with phenyl isothiocyanate to give **10** [21%, mp 126–129° (lit.[11] mp 129.5–130°)]. In the second step, **10** was oxidized with bromine in acetic acid to give **8** [53%, mp 197–199° (lit.[11] mp 203–203.5°)]. The NMR and ir spectra of this material are identical with those of **8** obtained from **1** and phenyl isothiocyanate.

Reaction of Phenyldimedonyliodone (1) with Thiourea. A solution of **1** (10.25 g, 29.95 mmol) in CH_2Cl_2 (60 ml) and a solution of thiourea (2.27 g, 29.82 mmol) in absolute ethanol (60 ml) were mixed and allowed to stir for 15 hr at room temperature. The solvents were subsequently evaporated in vacuo, and a red-orange solid remained.

Purification and Characterization of 13. The crude solid was recrystallized from absolute ethanol (150 ml), and two crops of white crystals were obtained: yield 4.23, 0.44 g (67%); mp 170°; ^1H NMR (Me_2SO-d_6) δ 0.98 (s, 6 H), 2.23 (s, 4 H), 3.7 (very broad "singlet," 2 H, H_2O of hydration), 8.28 (very broad singlet, 4 H, $-NH_2$); ir (KBr) 1645 cm^{-1} ($C{=}N^+H_2$); uv (CH_3OH)λ_{max} 266 nm (ϵ 19607).

Anal. Calcd for $C_9H_{14}N_2O_2S{\cdot}H_2O$: C, 46.53; H, 6.94; S, 13.80. Found: C, 46.54; H, 6.93; S, 13.91.

This compound is insoluble in CH_3CN, $CHCl_3$, ether, acetone, and cyclohexane, and for that reason, Me_2SO-d_6 was chosen as the NMR solvent. Sometimes the H_2O resonance appears to be fairly sharp and sometimes very broad. We have no explanation for this behavior.

Registry No.—**1**, 35024-12-5; **8**, 56995-06-3; **9**, 56995-07-4; **10**, 7721-63-3; **13**, 56995-08-5; phenyl isothiocyanate, 103-72-0; iodobenzene, 591-50-4; methyl isothiocyanate, 556-61-6; H_2S, 7783-06-4; thiourea, 62-56-6.

References and Notes

(1) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 3959 (1968).
(2) W. H. Pirkle and G. F. Koser, *J. Am. Chem. Soc.*, **90**, 3598 (1968).
(3) W. Ando, S. Kondo, and T. Migita, *J. Am. Chem. Soc.*, **91**, 6516 (1969).
(4) W. Ando, T. Yagihara, S. Kondo, K. Nakayama, H. Yamato, S. Nakaido, and T. Migita, *J. Org. Chem.*, **36**, 1732 (1971).
(5) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Am. Chem. Soc.*, **94**, 3870 (1972).
(6) W. A. Sheppard and O. W. Webster, *J. Am. Chem. Soc.*, **95**, 2695 (1973).
(7) For a discussion of the involvement of halonium ylides in carbene reactions, see A. P. Marchand and N. MacBrockway, *Chem. Rev.*, **74**, 431 (1974).
(8) E. Gudrinietse, O. Neiland, and G. Vanag, *J. Gen. Chem. USSR (Engl. Transl.)*, **27**, 2777 (1957).
(9) G. F. Koser and S.-M. Yu, *J. Org. Chem.*, **40**, 1166 (1975).
(10) O. Neiland and G. Vanag, *Proc. Acad. Sci. USSR, Chem. Sect.*, **130**, 19 (1960).
(11) G. Barnikow, *J. Prakt. Chem.*, **32**, 259 (1966).
(12) S. V. Kalnin and O. Neiland, *J. Org. Chem. USSR (Engl. Transl.)*, **7**, 1668 (1971).
(13) See C. J. Pouchert, "The Aldrich Library of Infrared Spectra", Aldrich Chemical Co., 1970, Spectrum 361B.