of polystyrene. Nuclear magnetic resonance spectra were recorded with a Varian T-60 spectrometer. Signals are reported as the chemical shift downfield from tetramethylsilane (TMS) in parts per million (ppm) of the applied field. The multiplicity of the peak is abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; and multiplet, m. Coupling constants are reported in hertz. Melting points were determined on a calibrated Thomas capillary melting point apparatus. Melting points are not corrected.

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Iodonium Ylides. Reactions of Phenyldimedonyliodone with Diphenylketene and Phenyl Isocyanate

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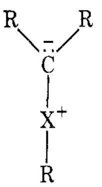
While the chemistry of phosphorous, nitrogen, and sulfur ylides has been studied extensively,[1] little is known of the halogen ylides. Halonium ylides of general structure 1 have been proposed when various carbenes are generated in the presence of alkyl and aryl halides,[2] but their high reactivity has largely precluded their isolation and study. We know of only one report concerning the formation of stable halonium ylides by carbene trapping. Sheppard and Webster[3] found that the thermal decomposition of 3,5-dicyanodiazoimidazole (2) in chlorobenzene, bromobenzene, or iodobenzene gave the corresponding chloronium, bromonium, and iodonium ylides **3a**, **3b**, and **3c**. Some iodonium ylides have also been prepared by a different method which involves the treatment of various β-diketones and β-keto esters with aryliodoso compounds.[4,5] For example, phenyldimedonyliodone (4),[6,7] one of the most stable iodonium ylides, has been synthesized in high yield by condensation of iodosobenzene with dimedone in the presence of acetic anhydride.[5] However, chemical studies on 4 have been limited to its reactivity toward highly electrophilic agents and to its proclivity for nucleophilic cleavage and thermal decomposition and rearrangement.[6,8] We were, therefore, prompted to initiate a systematic study of 4 in order to *begin* to elaborate the chemical properties of halonium ylides. In this note, we describe reactions of 4 with two representative electrophilic heterocumulenes.



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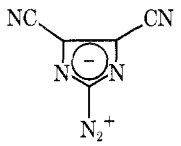

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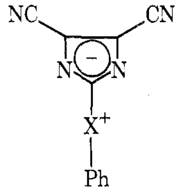
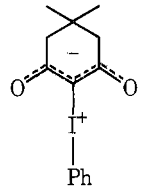


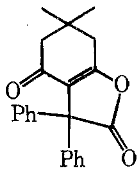
3a, X = Cl
b, X = Br
c, X = I



4

When phenyldimedonyliodone (4) was allowed to react with diphenylketene in dichloromethane at room temperature, lactone 5 and ketene acetal 6 were *isolated* in yields of 32 and 44% by column chromatography on Florasil. Iodobenzene is also formed in this reaction, and, in a control study, the yield of iodobenzene was determined by GLC analysis to be 99%. The structures of 5 and 6 were initially deduced from spectral (ir, NMR, uv, mass) and analytical (C, H) data.

The mass spectra of both compounds show the expected molecular ion peaks at m/e 332. However, while the parent ion peak in the spectrum of 5 is also the base peak, the base peak in the spectrum of 6 is at m/e 166 and must be that of a fragment ion derived from scission of the exocyclic carbon–carbon double bond. The ^{1}H NMR spectra of 5 and 6 are similar in that each exhibits a six-hydrogen singlet, a pair of two-hydrogen singlets, and a ten-hydrogen phenyl resonance. Their uv spectra are also similar, but the absorption maximum (α,β-unsaturated ketone) in the spectrum of 6 is red shifted by 11 mμ relative to that of 5. The ir spectrum of 5 exhibits carbonyl bands at 5.50 (lactone) and 5.99 μ (ketone) while the ir spectrum of 6 shows a carbonyl band at 6.01 μ (ketone) and exocyclic double-bond absorption at 5.78 μ. Finally, the melting point of 6 is 60° higher than that of 5, presumably because of its greater molecular symmetry.



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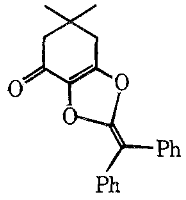
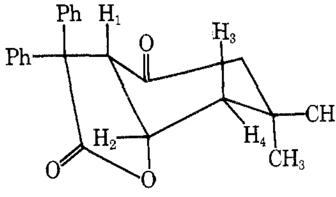


6



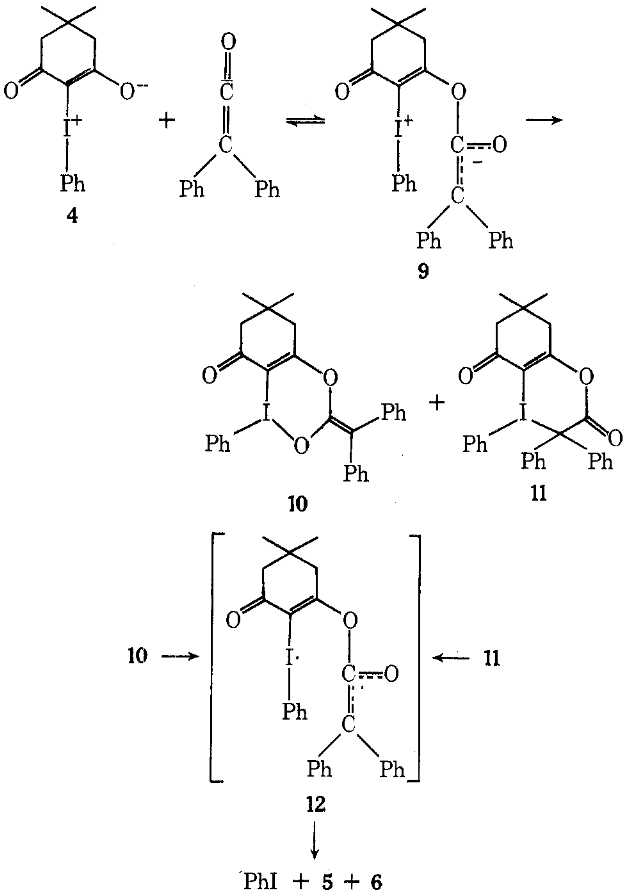
7

The structure assigned to 5 was confirmed by its catalytic hydrogenation in 54% yield to the saturated lactone 7, which was in turn characterized by its elemental composition (C, H) and spectra (ir, NMR, uv, mass). In particular, the ir spectrum of 7 exhibits a carbonyl band at 5.72 μ as expected for a saturated γ-lactone while the uv spectrum shows only benzenoid absorption at 259 mμ (ϵ 633). The ^{1}H NMR spectrum of 7 exhibits *two* methyl singlets at δ 0.87 and 0.81, a ten-line multiplet at δ 5.0 (H-2, $J_{2,3} \simeq 11$, $J_{2,1} \simeq 8.5$, $J_{2,4} \simeq 6.5$ Hz), a doublet at δ 4.42 (H-1, $J_{1,2} \simeq 8.5$ Hz), and complex multiplets for the phenyl and methylene hydrogens. The doublet resonance for H-1 at δ 4.42 may seem anomalously downfield for a proton in that environment. However, inspection of Dreiding models indicates very clearly that H-1 lies in the deshielding region of one of the benzene rings.

The structure assigned to 6 was confirmed by oxidative cleavage of the exocyclic carbon–carbon double bond. When 6 was allowed to react with ozone and treated subsequently with basic hydrogen peroxide, benzophenone was isolated in 66% yield and characterized as its 2,4-dinitrophenylhydrazone. The ketene acetal proved remarkably resistant to hydrolysis. Even when 6 was warmed to dissolution in concentrated sulfuric acid and poured into water, it was recovered unreacted in 86% yield. The inertness of 6 toward hydrolytic cleavage may reflect the aromaticity of its conjugate acid 8.

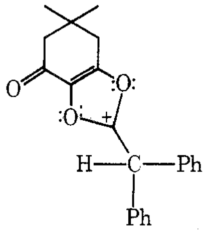
The production of iodobenzene, lactone 5, and acetal 6 is a consequence of *formal* 1,3-addition of the dimedonyl unit in 4 to either the carbon–carbon or carbon–oxygen double bond of diphenylketene. There are not sufficient data to allow commitment to any one of several possible mechanisms for this reaction, but we would like to discuss specifically the mechanism shown in Scheme I. It seems reasonable to presume that the reaction is initiated by nucleophilic attack of **4** on diphenylketene to give betaine **9**. Although **5** and **6** might conceivably arise from **9** by direct displacement of iodobenzene from vinyl carbon, such a process seems unlikely. SN1 displacements at vinyl carbon are known,[9] but, in the case of **9**, this would require the formation of a *cyclic* vinyl cation with positive charge adjacent to carbonyl carbon. There also seems to be no special driving force for an addition–elimination sequence. The formation of iodine(III) heterocycles **10** and **11** by cyclization of betaine **9** and their subsequent homolytic decomposition through diradical **12** is a plausible source of the observed products. Such a reaction sequence finds precedent in a detailed study of iodine(III) compounds conducted by Beringer, Dehn, and Winicov.[10] For example, when diphenyliodonium chloride (100 mmol) was treated by those workers with ethylmagnesium bromide (200 mmol) in ether at −5°, the final products were iodobenzene (80 mmol), biphenyl (5 mmol), iodoethane (20 mmol), ethylbenzene (15 mmol), and benzene (95 mmol).[10]

Scheme I



When phenyldimedonyliodone (**4**) was allowed to react with phenyl isocyanate in dichloromethane at room temperature, only one "cycloadduct", assigned the oxazolinone structure **13**, was isolated in 44% yield. The structure of **13** was deduced from its elemental composition (C, H, N) and spectra (ir, NMR, uv). In particular, the ir spectrum of **13** exhibits two carbonyl bands at 5.94 (ketone) and 5.63 μ (azalactone).

If a homolytic decomposition mechanism such as that depicted in Scheme I were responsible for the genesis of **13**, the absence of the isomeric product **14** seems anomalous. We will, however, defer specific considerations regarding mechanism to a future report.



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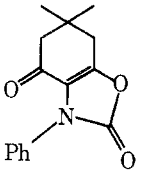
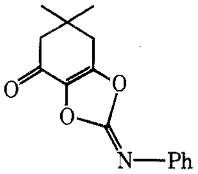


13



14

Experimental Section

General. NMR spectra were recorded on a Varian Model A-60 NMR spectrometer (relative to internal TMS), infrared spectra on a Perkin-Elmer Model 337 spectrophotometer, and ultraviolet spectra on a Cary 17 uv–visible–ir spectrophotometer. Mass spectra were recorded on a Du Pont 21-110C spectrometer. Peaks of fragment ions with intensities greater than 30% that of the base peak are reported. 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. Diphenylketene was prepared according to the method of Darling and Kidwell.[11] We thank Dr. Stephen D. Darling for a gift of some diphenylketene.

Reaction of Phenyldimedonyliodone (4) with Diphenylketene. A solution of diphenylketene (9.06 g, 46.6 mmol) and phenyldimedonyliodone (8.62 g, 25.2 mmol) in CH_2Cl_2 (80 ml) was allowed to stir for 5 days at room temperature. The CH_2Cl_2 was then evaporated *in vacuo*, and the remaining material resolved by column chromatography on Florisil (230 g). Twenty-five fractions of *ca.* 300 ml each were collected as the elution solvent was gradually changed from cyclohexane (fractions 1–9) to ether (fractions 10–21) to ethanol (fractions 22–25). Certain fractions were then combined, and the solvent was removed. The residues were triturated with cyclohexane or ether and finally analyzed by NMR spectroscopy. Fractions 3–12 yielded 2.686 g (32%) of lactone **5** as a crude yellow solid, and fractions 13–21 yielded 3.721 g (44%) of ketene acetal **6** as a crude white solid. Fractions 22–25 gave ca. 4 g of a brown, tacky substance apparently derived from diphenylketene.

Purification and Characterization of 5. The crude lactone **5** was recrystallized from cyclohexane–dichloromethane (2:1 v/v) as white needles and plates (2.307 g): mp 136–137°; ir ($CHCl_3$) 5.50 (lactone C=O), 5.99 and 6.07 μ (ketone C=O); NMR ($CDCl_3$) δ 7.28 (s, 10 H), 2.60 (s, 2 H), 2.32 (s, 2 H), 1.13 (s, 6 H); uv (CH_3OH) 252.5 mμ (ϵ 8.991×10^3); mass spectrum (70 eV) *m/e* (rel intensity) 332 (100), 304 (48), 303 (59), 178 (31); mol wt 332 (calcd, 332); (M + 1)/M, 24.11% (calcd, 24.16%).

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.32; H, 6.14.

Purification and Characterization of 6. The crude ketene acetal **6** was recrystallized from cyclohexane–dichloromethane (2:1 v/v) as fine white needles (2.973 g): mp 196–197°; ir ($CHCl_3$) 6.01 (C=O), 5.78 μ (exocyclic C=C); NMR ($CDCl_3$) δ 7.38 (m, 10 H), 2.78 (s, 2 H), 2.34 (s, 2 H), 1.16 (s, 6 H); uv (CH_3OH) 263 mμ (ϵ 1.0101×10^4); mass spectrum (70 eV) *m/e* (rel intensity) 332 (40), 166 (100), 165 (60); mol wt 332 (calcd, 332); (M + 1)/M, 23.1% (calcd, 24.16%).

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.31; H, 5.81.

Hydrogenation of 5. A solution of lactone **5** (1.752 g, 5.27 mmol) in ethyl acetate (40 ml) over 10% palladium on charcoal (0.351 g) was allowed to stir under hydrogen for 1 week at room temperature and atmospheric pressure. The catalyst and solvent were subsequently removed, leaving 1.973 g of a viscous liquid which partially solidified upon standing. Resolution of the crude product was effected by column chromatography on Florisil (150 g) as the elution solvent was gradually changed from cyclohexane to ether to ethyl acetate. Two cyclohexane fractions, two ether fractions, and one ethyl acetate fraction were collected. The solvent was removed from each fraction and the remaining material subjected to NMR analysis. Fraction 1 (0.453 g) was a wet solid which, after trituration with cyclohexane, yielded 0.308 g of lactone **7**. Fraction 2 (0.643 g) was fairly pure **7**. The crude solids from fractions 3 (0.250 g), 4 (0.106 g), and 5 (0.235 g) were not identified. Thus, the yield of lactone **7** was 0.951 g (54%).

Purification and Characterization of 7. The crude lactone **7** (0.951 g) was recrystallized from cyclohexane–dichloromethane

(1:1 v/v), yield 0.851 g: mp 164–166°; ir (KBr) 5.72 (lactone C=O), 5.91 μ (ketone C=O); NMR ($CDCl_3$) δ 7.85, 7.22 (complex multiplets, aromatic hydrogens), 5.0 (ten-line multiplet, H-2, $J_{2,3} \simeq 11.0$, $J_{2,1} \simeq 8.5$, $J_{2,4} \simeq 6.5$ Hz), 4.42 (d, H-1, $J_{1,2} \simeq 8.5$ Hz), 1.78 (m, $-CH_2-$ hydrogens), 0.87 (s, $-CH_3$), 0.81 (s, $-CH_3$); uv (CH_3OH) λ_{max} 259 mμ (ϵ_{max} 633), shoulders at 253 (567), 264 (560), and 270 (365); mass spectrum (70 eV) *m/e* (rel intensity) 334 (100), 290 (38), 289 (34), 274 (36), 206 (93), 205 (42), 166 (37), 91 (32); mol wt 334 (calcd, 334); (M + 1)/M, 26.9% (calcd, 24.3%).

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.32; H, 6.51.

Ozonation of 6. A solution of ketene acetal **6** (0.126 g, 0.0379 mmol) and pyridine (5 ml) in dichloromethane (250 ml) was cooled to 0° and subjected to an ozone stream for 30 hr. Sodium hydroxide (5%, 40 ml) and hydrogen peroxide (30%, 2 ml) were then added, and the resulting two-phase mixture was refluxed for 16 hr. The aqueous and organic layers were then separated, and the aqueous layer was extracted with dichloromethane (2 × 100 ml). The extracts and the organic layer were combined, dried ($MgSO_4$), and concentrated in vacuo, leaving a yellow solid (0.086 g) shown by NMR analysis to consist of benzophenone and other unidentified materials. When an attempt to isolate benzophenone by preparative TLC failed, the crude product was dissolved in 95% ethanol (10 ml) and treated with fresh DNP reagent [2,4-dinitrophenylhydrazine (0.2 g), H_2O (1.5 ml), concentrated H_2SO_4 (1 ml), and 95% ethanol (5 ml)]. The resulting solution, upon standing overnight at room temperature, yielded an orange solid which was isolated by filtration and washed with cold 95% ethanol, wt 0.131 g. The crude solid was then purified by column chromatography on neutral alumina with 1:1 (v/v) cyclohexane–ether (400 ml) followed by ether (600 ml) as the elution solvents; 0.091 g of an orange powder (mp 234–236°) with an infrared spectrum identical with that of authentic benzophenone 2,4-dinitrophenylhydrazone was obtained (yield 66%). Recrystallization of this material from 1:1 (v/v) ethyl acetate–ethanol gave 0.083 g of orange crystals, mp 236–236.5° (lit.[12] mp 239°).

Reaction of 4 with Diphenylketene. Yield of Iodobenzene. A solution of diphenylketene (1.64 g, 8.44 mmol) in CH_2Cl_2 (10 ml) was added to a solution of **4** (1.71 g, 5.00 mmol) in CH_2Cl_2 (10 ml), and the resulting solution was diluted volumetrically with CH_2Cl_2 to 25 ml. The reaction mixture was allowed to stand for 4.5 days at room temperature. At the end of this time, a 10-ml volumetric aliquot was removed, added to 0.1781 g (1.327 mmol) of durene, and subjected to GLC analysis. Three separate injections gave the peak area ratios (as determined by planimeter integration) shown below.

Injection	Durene/iodobenzene
1	0.765
2	0.761
3	0.791

A known mixture of durene (1.96 mmol) and iodobenzene (2.07 mmol), when subjected to similar analysis, gave the following peak area ratios.

Injection	Durene/iodobenzene
1	1.078
2	1.129
3	1.075

Thus, the durene/iodobenzene peak area ratio must be multiplied by a factor of 0.867 to give the correct durene/iodobenzene mole ratio.

The yield of iodobenzene was, therefore, 99%.

Reaction of Phenyldimedonyliodone (4) with Phenyl Isocyanate. A solution of **4** (11.12 g, 32.5 mmol) and phenyl isocyanate (7.8 g, 65.5 mmol) in CH_2Cl_2 (120 ml) was allowed to stir for 4.5 days at room temperature. The CH_2Cl_2 was then evaporated in vacuo and the remaining wet, brown cake resolved by column chromatography on Florisil (225 g). Twenty-one fractions of ca. 300 ml each were collected as the elution solvent was gradually changed from cyclohexane (fractions 1–2) to ether (fractions 3–12) to CH_2Cl_2 (fractions 13–16) to ethanol (fractions 17–21). Various fractions were then combined, the solvent was removed, and the residues were triturated with ether and subjected to NMR analysis. Fractions 4–7 yielded 2.81 g of crude oxazolinone **13** as a white to faintly yellow solid. Fractions 9–14 yielded 4.85 g of a white solid (mp ~235°) identified as diphenylurea, and fractions 17–21 gave 2.65 g of unreacted **4**. The yield of **13** based on unrecovered **4** was 44%.

Purification and Characterization of 13. The crude oxazolinone **13** was recrystallized from cyclohexane–dichloromethane (1:1 v/v) as white needles: mp 122–123°; ir ($CHCl_3$) 5.63 (C=O), 5.94 μ (ketone C=O); NMR ($CDCl_3$) δ 7.37 (m, 5 H), 2.64 (s, 2 H), 2.37 (s, 2 H), 1.17 (s, 6 H); uv (CH_3OH) 276 mμ (ϵ 9.802 × 10^3).

Anal. Calcd for $C_{15}H_{15}O_3N$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.16; H, 5.83; N, 5.38.

Attempted Hydrolyses of 6. A. A solution of **6** (0.5 g, 1.50 mmol) in glacial acetic acid (25 ml) and water (2.5 ml) was heated to boiling for 10 min. The reaction mixture was then allowed to cool, poured into water (100 ml), and extracted with ethyl acetate. The extract was dried ($MgSO_4$) and concentrated in vacuo, leaving 0.44 g (88%) of unreacted **6**.

B. A solution of **6** (1.2 g, 3.61 mmol) in dioxane (180 ml), water (19 ml), and concentrated hydrochloric acid (1 ml) was warmed on a steam bath for 2 hr. The dioxane was subsequently removed by evaporation at reduced pressure, and the remaining aqueous solution was extracted with ether. The ethereal solution was isolated, dried ($MgSO_4$), and concentrated in vacuo, leaving 1.01 g (84%) of unreacted **6**.

C. A solution of **6** (0.8 g, 2.41 mmol) in dioxane (100 ml), water (40 ml), and concentrated sulfuric acid (10 ml) was heated for 22 hr, and the reaction mixture was subsequently extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated in vacuo, leaving 0.71 g (89%) of unreacted **6**.

D. Ketene acetal **6** (0.3 g, 0.91 mmol) was added to concentrated sulfuric acid, and the mixture was warmed until solution was effected. The solution was then poured into water (100 ml) and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated in vacuo, leaving 0.26 g (87%) of unreacted **6**.

Synthesis of Phenyldimedonyliodone (4). Although the synthesis of **4** has been thoroughly described by other workers,[5,6] we employed the slightly modified procedure which follows.

A solution of 5.5 g (39.2 mmol) of dimedone (Eastman Chemical Co.) and 12 g (37.3 mmol) of iodosobenzene diacetate (Eastman Chemical Co.) in CH_2Cl_2 (200 ml) was allowed to stir for 15 min at room temperature. The reaction mixture was then washed with two 150-ml portions of 5% KOH and two 100-ml portions of saturated aqueous sodium chloride, filtered through anhydrous $MgSO_4$, and concentrated to dryness in vacuo. The pale yellow solid residue was triturated with ether and ultimately yielded 10.4 g (81%) of **4** as a white powder, mp 130° dec.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also wish to thank Dr. Stephen D. Darling and Dr. William G. Kofron for helpful discussions.

Registry No.—**4**, 35024-12-5; **5**, 54166-39-1; **6**, 54166-40-4; **7**, 54166-41-5; **13**, 54166-42-6; diphenylketene, 525-06-4; benzophenone 2,4-DNP, 1733-62-6; iodobenzene, 591-50-4; phenyl isocyanate, 103-71-9; diphenylurea, 102-07-8; dimedone, 126-81-8; iodosobenzene diacetate, 3240-34-4.

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