that the effect of diamagnetic anisotropy in allenes is small. First, there appears to be no large effect which can be ascribed to anisotropy at the α position. Indeed, the rather irregular chemical-shift changes which do occur at this position may be due largely to the effects of the conformation of the ring. Second, the chemical shift of the alkene carbons of *cis*-cyclononene[11] do not differ significantly from that of the alkene unit of cyclonona-1,2,6-triene.

Conclusions

The present results generally confirm and extend earlier conclusions[5-7] regarding the magnetic anisotropy of the triple bond. The shifts observed show variations which are in general accord with the McConnell equation. However, the observed shifts are several times larger than those observed in proton chemical shifts.

The carbon spectra of the alkenes and allenes do not show large effects which can unambiguously be assigned to magnetic anisotropy. Owing to limitations of the theoretical models of such systems and to the sparse data from proton nmr studies of these compounds, the recognizable effects which do occur are difficult to evaluate and assign to specific causes.

Registry No.—**1**, 871-84-1; **2**, 16387-71-6; **3**, 5601-68-3; **4**, 872-21-9; **5**, 1540-80-3; **6**, 39805-79-3; **7**, 7158-20-5; **8**, 14538-94-4; **9**, 4634-66-6; **10**, 39805-82-8; **11**, 39805-83-9; **12**, 6675-65-6; **13**, 39805-85-1; **14**, 628-41-1; **15**, 111-78-4; **16**, 6108-60-7; **17**, 1123-11-1; **18**, 1502-42-7; **19**, 3451-55-6; **20**, 5601-67-2; **21**, 7129-53-5.

Cycloaddition of Diphenylketene to Some C=N Heterocycles. Structural Assignment and Reactions of Adducts[1]

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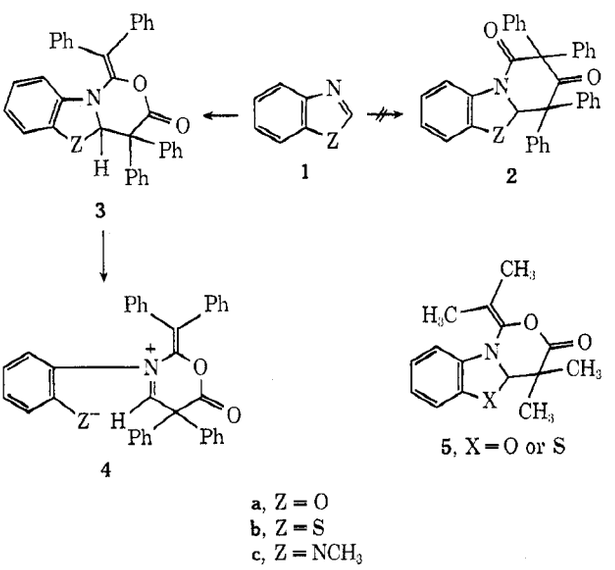
The cycloaddition reactions of diphenylketene to some C=N heterocycles have been reexamined and the adducts are assigned oxazinone (**3** or **4**) rather than amido ketone structures **2**. The reaction of **4** with hydrazine yielded pyrazolinone **7**, whereas sodium methoxide produced the ring-opened ester **6**.

As part of our interest in the cycloaddition reactions of ketenes to olefins and to heterocycles,[2] we investigated the reaction of some heterocyclic imines with diphenylketene.

The cycloaddition of ketenes to imines is known to proceed with formation of 1:1 or of 2:1 adducts. In the latter case six-membered ring products were isolated and assigned structures that ranged from amido ketones[3] or lactones (oxazinones)[4] to dioxazines.[2d] The factors influencing the type of cycloadduct formed have not been examined.

The reactions of diphenylketene with 2-methylthiazoline, *N*-methylimidazole, benzoxazole, benzothiazole, and *N*-methylbenzimidazole were reported by Kimbrough,[3] who found that these heterocycles added to diphenylketene in a 1:2 ratio to give adducts to which he assigned an amido ketone structure, *e.g.*, **2**. These results are surprising in view of the formation of oxazinones from the cycloaddition of dimethylketene with C=N heterocycles.[4] The infrared bands at 1770 cm^{-1} reported by Kimbrough for the adducts from benzoxazole and benzothiazole do not agree with an amido ketone structure **2**. Such adducts are expected to show two strong carbonyl bands at 1710 and 1680 cm^{-1}. In the course of our cycloaddition studies of diphenylketene we reexamined the reported reactions and would like to correct the previous structure assignment and to shed light on some interesting ring-opening reactions that occur in these heterocyclic systems.



a, Z = O
b, Z = S
c, Z = NCH_3

Results and Discussion

We were able to reproduce the cycloaddition of diphenylketene to the heterocycles stated above including the infrared data. The diphenylketene adducts from benzoxazole and benzothiazole (**1**, Z = O and S) showed strong carbonyl absorptions at 1770 cm^{-1} and medium bands at 1665 and 1640 cm^{-1}, in addition to strong bands at 1130 cm^{-1} indicative of a

(1) Cycloadditions. XI. For paper X in this series see A. Hassner, A. S. Miller, and M. J. Haddadin, *J. Org. Chem.*, **37**, 2682 (1972).

(2) (a) A. Hassner, V. R. Fletcher, and D. P. G. Hamon, *J. Amer. Chem. Soc.*, **93**, 264 (1971); (b) A. Hassner, and V. R. Fletcher, *Tetrahedron Lett.*, 1071 (1970); (c) *ibid.*, 5053 (1970); (d) A. Hassner, A. S. Miller, and M. J. Haddadin, *ibid.*, 1353 (1972).

(3) R. D. Kimbrough, Jr., *J. Org. Chem.*, **29**, 1242 (1964).

(4) (a) J. C. Martin, K. C. Brannock, R. D. Burpitt, P. Glenn Gott, and V. A. Hoyle, Jr., *J. Org. Chem.*, **36**, 2211 (1971); (b) M. A. Shah and G. A. Taylor, *J. Chem. Soc. C*, 1651 (1970), and other papers in the series; (c) R. Huisgen, B. A. Davis, and M. Morikam, *Angew. Chem., Int. Ed. Engl.*, **7**, 826 (1968).

vinyl ester. The adduct from imidazole or *N*-methylbenzimidazole displayed strong absorptions at 1750 cm^{-1} and very weak bands at 1600 cm^{-1}.

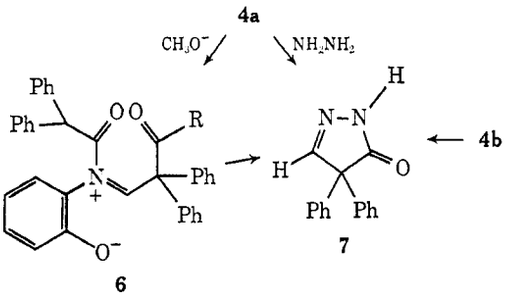
The above facts lead us to conclude that the cycloaddition adducts from **1** and diphenylketene have an oxazinone structure **3**. Analogous oxazinone structures (*e.g.*, **5**) have been assigned to the adducts of dimethylketene to **1a** and **1b**[4a] as well as to ketene adducts of imines and C=N heterocycles.[4]

Interestingly, the nmr spectra of the adducts of **1a** and **1b** with diphenylketene did not show a singlet for the proton at the ring junction in the expected region of τ 4.5–6,[5] whereas the spectrum of the diphenylketene adduct from **1c** and that from *N*-methylimidazole each gave a singlet (1 H) near τ 4.9. A careful inspection of the aromatic region of the adducts from **1a** and **1b** revealed a sharp singlet (1 H) at τ 3.2, which retained its sharpness and shifted downfield on addition of $Eu(fod)_3$ reagent. This low-field absorption strongly suggests that the structure of the diphenylketene adducts to **1a** and **1b** are best represented by the ylides **4a** and **4b**. The adduct derived from **1c** is assigned the ring-closed structure **3c**. These assignments are further corroborated by the position of the methine absorption in the nmr spectra of related systems (see below).[5] The ^{13}C nmr spectrum of **4a** showed two signals at 164 and 156 ppm (downfield from TMS), whereas the adduct **3c** showed one signal at 170 ppm (C=O), with the rest of the signals between 30 and 140 ppm. The low-field singlet at 156 ppm, which was more intense than that at 164 ppm (C=O), is attributable to the iminium carbon in **4**.

An examination of the molecular model of **3** indicates that, in practically all conformations, there exists a most severe interaction between the ortho-disubstituted aromatic ring and the vinylic phenyl system. Such interaction is markedly minimized in structure **4** owing to increased flexibility. Moreover, the conversion of **3** into **4** is facilitated by the good leaving group property of the phenoxide and thiophenoxide anions. It appears that ring cleavage of **3** to product **4** requires that both of the above factors be operative. Such an assumption is supported by the fact that adduct **3c**, which lacks good leaving group, exists entirely in the tricyclic structure (singlet at τ 4.9) in spite of the presence of steric interaction among the phenyl groups. Secondly, the adducts of dimethylketene to benzoxazole and benzothiazole[4a,5b] showed a singlet (1 H) at τ 4.5–4.8 and therefore possess structure **5**. In this case, less steric interference is experienced by the smaller methyl substituents. The mass spectra of adducts **3c**, **4a**, and **4b** showed weak peaks at $M^+ - CO$ and strong peaks at $M^+ - Ph_2C{=}C{=}O$ (194).

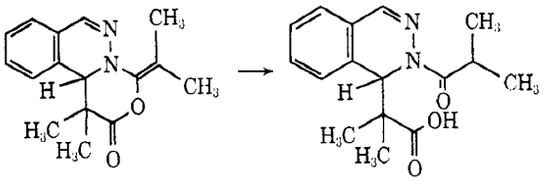
The structure of adduct **4a** was corroborated by the following chemical transformations. Pyrolysis of the adduct yielded benzoxazole and diphenylketene. Whereas treatment of **4a** with methanolic sodium methoxide gave methyl ester **6** (R = OCH_3); reaction with hydrazine afforded diphenylacetylhydrazide and pyrazolinone **7**. The latter was also obtained by refluxing a methanolic solution of **6** (R = OCH_3) with hydrazine, or by treatment of **4b** with hydrazine.

(5) (a) T. A. Crabb and R. F. Newton, *Tetrahedron Lett.*, 3361 (1971). (b) We are grateful to Dr. J. C. Martin for supplying us with the nmr spectra of these adducts.



6 7

The formation of **7** most likely involves an attack of hydrazine on the carbonyl carbon of **4a** followed by another attack on the iminium carbon, resulting in ring closure. The possibility that the reaction proceeded by a reverse of the above order was ruled out on the basis of the fact that **4a** reacted with *unsym*-dimethylhydrazine to give **6** [R = $NHN(CH_3)CH_3$]. Treatment of the latter with hydrazine gave **7**. Product **6** (R = OCH_3) showed an M^+ peak at *m/e* 539 and two carbonyl bands at 1735 and 1680 cm^{-1} in the infrared. Its nmr spectrum exhibited three singlets at τ 6.3, 4.3, and 2.08, assigned to the methyl, benzylic hydrogen, and the iminium hydrogen, respectively. It is interesting to note that the iminium hydrogen in ester **6** has shifted downfield by about 1.1 ppm with respect to the proton in **4a**. This effect is probably analogous to the observation of Shah and Taylor,[4b] who reported that the ring junction proton in **8**, which appears at τ 5.2, shifts to 3.6 in the ring-opened **9**. The



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structure of pyrazolone **7** was consistent with its spectroscopic data.

Experimental Section[6]

4,4-Diphenyl-1-benzhydrylidene-5 methyl-4*H*-[1,3]oxazino-[4,3-*b*]benzimidazol-3-one (3c).—The title compound was prepared from *N*-methylbenzimidazole (**1c**) and diphenylketene according to ref 3: ir 1750 (s), 1600 (w), 1495, 1390, 1330, 1310, 1245, 1190, 1120 (s), 1080, 1070, 970, 780, 750, and 700 cm^{-1}; pmr τ 6.7 (s, 3 H), 4.9 (s, 1 H), 2.6–2.9 (m, 23 H), 2.05–2.2 (m, 1 H); ^{13}C nmr δ 170, 142, 136, 135.5, 132, 127, 126.8, 125.5, 120, 60.5, 30; mass spectrum M^+ 520, 492, 326, 297, 281, 215, 194, 166, 165, 152, 83, 77.

5,5-Diphenyl-2-benzhydrylidene-*N*-(*o*-phenoxide)-5*H*-[1,3]oxazonia-6-one (4a).—The title compound was prepared from **1a** according to Kimbrough's method:[3] ir 1770 (s), 1670 (m), 1600 (w), 1482, 1230, 1120, 1010, 760, and 705 cm^{-1}; pmr τ 3.2 (s, 1 H), 2.5–3.75 (m, 24). Addition of 45 and 90 mg of $Eu(fod)_3$ to a saturated solution of **4a** in $CDCl_3$ (1.5 ml) shifted the singlet at τ 3.2 to 3 and 2.9, respectively: ^{13}C nmr δ 164, 156.5, 140,

(6) All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were measured in Nujol on a Perkin-Elmer 457 grating spectrometer. Pmr spectra were taken in deuterated chloroform with TMS as an internal reference using a Varian A-60A spectrometer. ^{13}C nmr were measured in chloroform solution with TMS as an internal reference on a JEOL high-resolution JNM-PS-100 instrument. Mass spectra were determined on a Varian M. A. T. CH-5 instrument. Elemental analyses were performed at the Galbraith Laboratories, Inc.

136.5, 136, 135, 134.5, 128, 127, 126, 123.3, 120.5, 117.5, 108.6, 108, 95, 60; mass spectrum M+ 507, 479, 463, 333, 313, 285, 194, 178, 164, 165, 166, 152, 149, 119, 92, 83, 63.

5,5-Diphenyl-2-benzhydrylidene-*N*-(*o*-phenothioxide)-5*H*-[1,3]oxazonia-6-one (4b).—The title compound was prepared from **1b** according to ref 3: ir 1772 (s), 1640 (s), 1480, 1225, 1145, 1020, 760, and 710 cm^{-1}; pmr τ 3.82–4.02 (m, 1 H), 3.15 (s, 1 H), 2.5–3.52 (m, 23 H); ^{13}C nmr δ 166.9, 141.9, 140, 138.1, 137.9, 126.8, 127.0, 127.5, 128.0, 128.5, 129.5, 130.3, 124.9, 122.4, 121.3, 114.8, 112.8, 70.50, 62.54; mass spectrum M+ 523, 507, 495, 301, 195, 194, 163, 164, 165, 166, 167, 139, 135, 126, 115, 108, 97, 92, 77.

***o*-[*N*-(2,2-Diphenylacetyl)-2,2-diphenyl-2-carbomethoxy-*N*-acetiminium] Phenoxide (6).**—Oxazinone **4a** (0.3 g) was dissolved in hot dioxane (20 ml). Methanol (5 ml) containing sodium methoxide (0.3 g) was added to the solution, which turned yellowish. After heating on the steam bath for 5 min, the solution was filtered and the filtrate was diluted with water. The precipitated white solid was collected and treated with hot methanol. The dried white solid weighed 0.28 g, mp 174–176°. The analytical sample that melted at 180° was recrystallized from chloroform–methanol: ir 1738 (s), 1680 (2), 1490, 1265, 1235, 1215, 1180, 1160, 1100, 1025, 760, and 700 cm^{-1}; pmr τ 6.3 (s, 3 H), 4.3 (s, 1 H), 2.5–3.5 (m, 24 H), 2.1 (s, 1 H); mass spectrum M+ 539, 508, 480, 420, 314, 215, 197, 194, 165, 166, 167, 152, 119, 105, 85, 83, 77. *Anal.* Calcd for $C_{36}H_{29}O_4N$ (539.60): C, 80.13; H, 5.42; N, 2.60. Found: C, 80.14; H, 5.45; N, 2.75.

***o*-[*N*-(2,2-Diphenylacetyl)-2,2-diphenyl-2-(*N'*,*N'*-dimethylacylhydrazyl)-*N*-acetiminium] Phenoxide (6).**—Oxazinone **4a** (50 mg) was dissolved in excess *unsym*-dimethylhydrazine (3 ml) and the solution was heated on the steam bath until the solvent evaporated. The gummy residue was treated with ether and the resulting solid was collected (45 mg). The analytical sample was recrystallized from methanol–water and melted at 215°: ir 1680, 1650, 1485, 1260, 1220, 1150, 1030, 1020, 955, 770, and 710 cm^{-1}; pmr τ 7.6 (s, 6 H), 4.2 (s, 1 H), 2.5–3.6 (m, 24 H), 2.15 (s, 1 H); mass spectrum M+ 567, 508, 481, 448, 314, 287, 286, 255, 254, 225, 210, 194, 187, 167, 166, 165, 164, 152, 119, 77. *Anal.* Calcd for $C_{37}H_{33}O_3N_3$ (567.66): C, 78.28; H, 5.86; N, 7.40. Found: C, 78.36; H, 5.92; N, 7.14.

4,4-Diphenyl-5-pyrazolone (7) from 4a.—Oxazinone **4a** (1 g) was placed in hot methanol (15 ml). Hydrazine (95%, 5 ml) was added and the mixture was heated on the steam bath until all the solid (**4a**) dissolved. Water was added and the resulting white solid was collected by suction filtration, washed with water and methanol, and dried: 0.45 g; mp 207°; ir 3420, 1705, 1500, 1360, 840, 760, and 700 cm^{-1}; pmr τ 2.67 (s, 10 H), 2.05 (broad s, 1 H); mass spectrum M+ 236, 207, 194, 179, 166, 165, 152, 139, 102, 77.

Anal. Calcd for $C_{15}H_{12}ON_2$ (236.26): C, 76.25; H, 5.12; N, 11.86. Found: C, 76.06; H, 5.18; N, 11.76.

The mother liquor from the above reaction was left to stand overnight at room temperature. Diphenylacetylhydrazide precipitated, and was identified by comparison with an authentic sample: mp 134°; ir 3420, 1650, 1500, 1370, 1250, 1020, 1010, 750, 730, 700 cm^{-1}; nmr τ 2.6 (m, 2 H), 5.1 (s, 1 H), 3.7, (s, 10 H), 2.35 (m, 1 H).

Conversion of 6 into 4,4-Diphenyl-5-pyrazolone (7).—Product **6** [R = OCH_3 or $NHN(CH_3)_2$] (45 mg) was dissolved in hot methanol (10 ml). Hydrazine (95%, 2 ml) was added to the solution, which was left to stand at room temperature for 24 hr. Dilution with water and neutralization with hydrochloric acid resulted in the precipitation of 4,4-diphenyl-5-pyrazolone (10 mg), mp 207°.

The above procedure was also applied to the conversion of product **4b** into pyrazolone **7**.

Pyrolysis of Oxazinone 4a.—A sample of oxazinone **4a** was placed in a test tube and heated until it melted. The yellow liquid was shown (ir) to be a mixture of diphenylketene and benzoxazole by comparison with an authentic mixture. The identity of benzoxazole was confirmed by tlc on silica gel.

1-Methyl-5-benzhydrylidene-8,8-diphenyl-5*H*,8*H*-imidazo-[3,2-*c*]-1,3-oxazin-7-one (10).—The title compound was prepared from *N*-methylimidazole and diphenylketene according to ref 3. The product entraps solvent of crystallization (methanol): ir 1748 (s), 1600 (w), 1500, 1315, 1235, 1188, 1125 (s), 1050, 760, 750, and 710 cm^{-1}; pmr τ 6.9 (s, 3 H), 4.9 (s, 1 H), 3.35 (m, 1 H), 2.6–3.18 (m, 21 H); mass spectrum M+ 470, 276, 247, 194, 167, 165, 152, 83, 82.

Registry No.—**1a**, 273-53-0; **1b**, 95-16-9; **1c**, 1632-83-3; **3c**, 40110-18-7; **4a**, 40110-19-8; **4b**, 40110-20-1; **6** (R = OMe), 40317-83-7; **6** (R = $NHNMe_2$), 40110-21-2; **7**, 40110-22-3; **10**, 40110-23-4; diphenylketene, 525-06-4; sodium methoxide, 124-41-4; *unsym*-dimethylhydrazine, 57-14-7; hydrazine, 302-01-2; diphenylacetylhydrazide, 6636-02-8; *N*-methylimidazole, 616-47-7.

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The Chemistry of a Ketene–Sulfur Dioxide Adduct. II. Reactions with Heterocumulenes

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The reaction of ketenimines with ketene in anhydrous liquid sulfur dioxide gave substituted 1,2-oxathiane-4-one 2-oxides. The structures of these compounds were verified by both chemical and spectral methods. *p*-Tolylsulfonyl isocyanate reacted with ketene in liquid sulfur dioxide to yield *N*-(*p*-tolylsulfonyl)-3-thiazolidine-2,4-dione 1,1-dioxide. In addition, substituted 2,1,5-benzothiadiazepin-4-one 2-oxides were obtained from the corresponding *o*-phenylenediamine, ketene, and sulfur dioxide. The mechanisms of these reactions were believed to involve a ketene–sulfur dioxide adduct as a common intermediate. This reactive species was isolated and intercepted at low temperatures. During the course of this investigation, ketene was also found to react with *N*-sulfinylaniline to give *N*-phenyl-1,2-thiazetidin-3-one 1-oxide.

The cycloaddition of imines with ketene in liquid sulfur dioxide was described in earlier publications.[1,2] The mechanisms of the reactions discussed were believed to involve an intermediate formed from ketene and sulfur dioxide Although the isolation of the presumed adduct was not accomplished, its existence was detected by a low-temperature nmr study. Recently, we have observed other cycloadditions involving the ketene–sulfur dioxide adduct and certain heterocumulenes such as ketenimines. In addition, we offer further proof for the existence of such an adduct by its low-temperature isolation and interception with appropriate reagents.

(1) A. S. Gomes and M. M. Joullié, *Chem. Commun.*, 935 (1967).
(2) A. S. Gomes and M. M. Joullié, *J. Heterocycl. Chem.*, **6**, 729 (1969).