4,4a,5,7a-Tetrahydro-2-methylcyclopenta[*b*]thiopyran (4a) was prepared from endo ketone **1a**:[12] ^{1}H NMR (CCl_4) δ 1.87 (s, 3 H, CH_3C=), 2.03-2.33 (m, 4 H, CH_2), 2.73 (m, 1 H, angular H on C-4a), 4 (br d, J = 8 Hz, angular H on C-7a), 5.45-5.46 (m, 3 H); ^{13}C NMR ($CDCl_3$) (C numbering of **4** in Scheme II) δ 24.5 (Me on C-2), 31 (C-4), 39 (C-4a + C-5), 51.6 (C-7a), 122.5 (C-3), 131.5 and 133 (C-6 and C-7), 134.5 (C-2); mass spectrum, m/e 152 (M^+); IR (film) 3055, 3012, 1620 cm^{-1}.

Anal. Calcd for $C_9H_{12}S$: C, 70.99; H, 7.94; S, 21.06. Found: C, 71.16; H, 8.15; S, 21.26.

4,4a,5,7a-Tetrahydro-2,4-dimethylcyclopenta[*b*]thiopyran (4b) was prepared from endo ketone **1b**:[13] ^{1}H NMR (CCl_4) δ 1.1 (d, J = 7.5 Hz, 3 H), 1.85 (s, 3 H, CH_3C=), 2.05-2.33 (m, 3 H, CH_2, H on C-4), 2.97 (m, 1 H, angular H on C-4a), 4.1 (d, J = 9, 2 Hz, angular H or C-7a), 5.32-5.47 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 19 (Me on C-4), 24.5 (Me on C-2), 33.7 and 34.5 (C-4 and C-5), 46 (C-4a), 53.6 (C-7a), 128.5 (C-3), 131 and 134 (C-6 and C-7), 134.5 (C-2); mass spectrum, m/e 166 (M^+); IR (film) 3060, 3010, 1625 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.48; S, 19.28. Found: C, 72.25; H, 8.28; S, 19.29.

4,4a,5,7a-Tetrahydro-2,3-dimethylcyclopenta[*b*]thiopyran (4c) was prepared from ketone **1c**:[13] ^{1}H NMR (CCl_4) δ 1.85 (br s, 6 H, CH_3C=), 2.1-2.4 (m, 4 H, CH_2), 2.7-2.9 (m, 1 H, angular H on C-4a), 4 (br d, J = 8.5 Hz, angular H on C-7a), 5.4-5.7 (m, 2 H, CH=CH); ^{13}C NMR ($CDCl_3$) δ 21.5 and 21.8 (Me on C-2 and C-3), 39, 39.3, and 40 (C-4, C-4a, and C-5), 53 (C-7a), 124.5 (C-3), 131 and 132 (C-6 and C-7), 132.5 (C-2); mass spectrum, m/e 166 (M^+); IR (film) 3055, 1620 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.48; S, 19.28. Found: C, 72.21; H, 8.63; S, 19.08.

4,4a,5,7a-Tetrahydro-2,4,4-trimethylcyclopenta[*b*]thiopyran (4d) was prepared from endo thioketone **2d** by heating at 100 °C for 1 h: ^{1}H NMR (CCl_4) δ 1.02 (s, 3 H, CH_3 on C-4), 1.17 (s, 3 H, CH_3 on C-4), 1.8 (s, 3 H, CH_3C=), 2.1-2.3 (m, 3 H, CH_2 and H on C-4a), 4.1 (br d, J = 8.5 Hz, angular H on C-7a), 5.1 (br s, 1 H, H on C-3), 5.65 (br s, 2 H, CH=CH); ^{13}C NMR ($CDCl_3$) δ 24 (Me on C-2), 27.5 and 29 (Me on C-4), 33.5 (C-4), 34.5, 47 (C-4a), 51.5 (C-7a), 124.5 (C-3), 131.3 and 132 (C-6 and C-7), 134.5 (C-2); mass spectrum, m/e 180 (M^+); IR (film) 3050, 1620 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}S$: S, 17.18. Found: S, 17.89.

(*endo*-3,3-Dimethylbicyclo[2.2.1]hept-5-en-2-yl)ethanethione (2d) was prepared by sulfurization of endo ketone **1d**:[14] yield 95%; ^{1}H NMR δ 0.78 (s, 3 H, endo Me), 1.12 (m, 1 H), 1.47 (s, 3 H, exo Me), 1.62 (m, 1 H), 2.30 (m, 1 H), 2.6 (s, 3 H, CSMe), 3.03 (m, 1 H), 3.35 (m, 1 H), 5.95-6.5 (m, 2 H); ^{13}C NMR δ 23.3 and 32 (2 Me), 42.8, 44.3, 47.6, 50, 55.2, 55.5, 135.3 and 135.9 (C=C), 261.4 (C=S); mass spectrum, m/e 180 (M^+); UV (cyclohexane) λ_{max} 510 nm (ϵ 11). Anal. Calcd for $C_{11}H_{16}S$: C, 73.25; H, 8.94; S, 17.78. Found: C, 72.91; H, 8.82; S, 17.51.

Registry No. *endo*-**1a**, 824-60-2; *endo*-**1b**, 31062-12-1; *endo*-**1c**, 31062-15-4; *endo*-**1d**, 15780-45-7; *endo*-**2d**, 73367-89-2; **4a**, 73367-90-5; **4b**, 73367-91-6; **4c**, 73367-92-7; **4d**, 73367-93-8.

Reaction of Diphenylketene with 1-Methylbenzimidazole. A Reinvestigation

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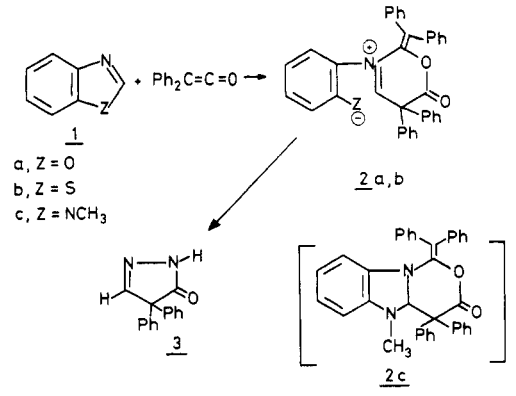
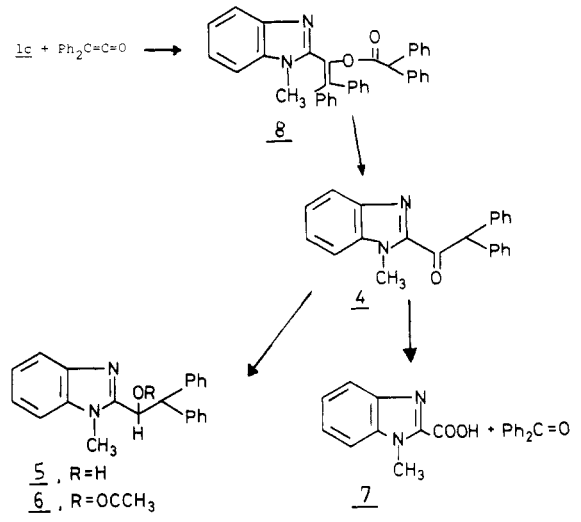
The reactions of diphenylketene with benzoxazole (**1a**), benzothiazole (**1b**), and 1-methylbenzimidazole (**1c**) were described first by Kimbrough.[1] The structures of these 1:2 adducts were revised later by Hassner and Haddadin,[2] who assigned them structures **2a-c**, respectively. We now present evidence that the adduct from **1c** has the enol acetate structure **8**.

Scheme I



Scheme II



Adducts **2a,b** were found to yield 4,4-diphenyl-5-pyrazolone (**3**) upon treatment with hydrazine[2] (Scheme I). We have now found that the adduct from **1c** gives a different product with hydrazine, which shows a strong carbonyl band at 1680 cm^{-1} and no infrared absorption in the N-H region. The NMR spectrum of the hydrazinolysis product consisted of two singlets at δ 3.88 (3 H) and 6.69 (1 H, exchangeable in $CDCl_3/D_2O$) in addition to the aromatic multiplet (14 H). The parent peak in the mass spectrum, m/e 326, corresponds to a molecular formula of $C_{22}H_{18}N_2O$. The same compound is obtained by the treatment of the adduct from **1c** with methanolic potassium hydroxide. Further evidence is presented in support of structure **4** for this product.

Reduction of ketone **4** with $NaBH_4$ gave alcohol **5** (m/e 328) (Scheme II) which displayed a broad band at 3100-3000 cm^{-1} and no carbonyl absorption; its NMR spectrum showed a singlet at δ 3.09 (3 H), two doublets at δ 4.47 and 5.32 (1 H each), and a multiplet at δ 6.6-7.1 (14 H). Acetylation of alcohol **5** with acetic anhydride yielded acetate **6** which, with base, was hydrolyzed to **5**. Oxidation of either ketone **4** or alcohol **5** with either chromic anhydride or manganese dioxide gave benzophenone as a major product. Ketone **4** was found to be sensitive to air oxidation, especially under basic conditions, and gave benzophenone. A Baeyer-Villiger oxidation of ketone **4** with *m*-chloroperbenzoic acid in acetic acid

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(2) Haddadin, M. J.; Hassner, A. *J. Org. Chem.* **1973**, *38*, 2650.

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yielded 1-methylbenzimidazole-2-carboxylic acid (7),[3] benzophenone, and traces of 1-methylbenzimidazole. Acid 7 is known to undergo decarboxylation readily even at room temperature.[4]

The above evidence establishes the structure of the hydrolysis product as ketone 4, and on the basis of this evidence, the structure of the adduct from the reaction of 1-methylbenzimidazole (1c) and diphenylketene should be 8 (1750 cm^{-1})[2] and not 2c.

The formation of vinyl ester 8 is related to the recent findings of Kohn, Gopichand, and Charumilind.[5]

Experimental Section[6]

Diphenylketene was prepared by either of two literature methods.[7a,b]

1-Methylbenzimidazole. The following method is a modification of that reported by Fisher[8] and Kimbrough.[1]

In a 1-L round-bottomed flask was dissolved benzimidazole (23.6 g) in methanol (150 mL). Methyl iodide (14.5 mL) was added, and the flask was tightly stoppered and swirled for 10 min. After the mixture had been allowed to stand at room temperature for 1 week, the brown solution was concentrated, and the residue was treated with chloroform (75 mL). The insoluble residue was filtered out. Evaporation of chloroform gave a solid which was dissolved in 10% sodium hydroxide. Addition of water to this solution resulted in two layers. Extraction with dichloromethane and evaporation of the dried dichloromethane gave an oily residue which was chromatographed on neutral alumina. 1-Methylbenzimidazole was eluted out in benzene. The product was hygroscopic and solidified at 0 °C: yield 6.97 g (26%); mp 60–61 °C (lit.[1] 60–61 °C); NMR δ 3.25 (s, 3 H), 6.80 (m, 3 H), 7.35 (m, 2 H); UV λ_{CCl_4} 281 nm (log ϵ 4.3), 274 (4.34), 266 (4.3); IR (neat) 1150, 1130, 1060, 1010, 890, 870, 750 cm^{-1}.

It was found that heating the reaction mixture increased the amount of side products at the expense of 1-methylbenzimidazole.

2-[1′-(Diphenylacetoxy)-2′,2′-diphenylethenyl]-1-methylbenzimidazole (8). The preparation and spectroscopic properties of 8 are found in ref 2 where the adduct was assigned structure 2c: UV λ_{EtOH} 303 nm (log ϵ 4.27), 262 (4.15). Anal. Calcd for $C_{36}H_{28}N_2O_2$: C, 83.0; H, 5.4; N, 5.4. Found: C, 82.7; H, 5.4; N, 5.2.

2-(Diphenylacetyl)-1-methylbenzimidazole (4). Benzimidazole 8 (1.5 g) was added to hot methanol (20 mL). Hydrazine (95%, 10 mL) was added, and the mixture was heated until the starting material dissolved. A saturated solution of sodium chloride was added. After the mixture was allowed to stand at room temperature for 1 h, the resulting solid was collected, washed with water, and dried. Diphenylacetylhydrazine precipitated from the mother liquor and was identified by comparison with an authentic sample[9] (mp 134 °C). Recrystallization of ketone 4 from methanol gave needles: mp 126–127 °C; 0.07 g (75%). Ketone 4 was obtained in 70% yield upon the heating of 8 in 10% methanolic potassium hydroxide for 1 h (1 g of 8 → 0.43 g of 4). Acidification of the basic mother liquor gave diphenylacetic acid (0.3 g). For 4: IR 1680, 1610, 1590, 1475, 1390, 1340, 1120, 1010, 1000, 750, 725, 700 cm^{-1}; NMR δ 3.88 (s, 3 H), 6.69 (s, 1 H), 6.85–7.25 (m, 13 H), 7.55 (m, 1 H); UV λ_{EtOH} 309 nm (log ϵ 3.95), 287 (4.02), 280 (4.03), 258 (4.06), 243 (4.09); mass spectrum, *m/e* 326, 194, 166, 152, 132, 131, 105, 77. Anal. Calcd for $C_{22}H_{18}N_2O$: C, 80.95; H, 5.56; N, 8.58. Found: C, 81.10; H, 5.63; N, 8.48.

2-(2′,2′-Diphenyl-1′-hydroxyethyl)-1-methylbenzimidazole (5) and Acetate 6. Ketone 4 (0.2 g) was dissolved in boiling methanol (10 mL), and sodium borohydride (0.2 g) was gradually added. The reaction mixture was allowed to stand at room temperature for 1 h, and the resulting solid was collected, washed with water, and recrystallized from methanol: yield 0.17 g (85%); mp 226–228 °C; IR 3100–3000 (broad band), 1620, 1600, 1450, 1400, 1287, 1220, 1095, 1080, 922, 750, 705 cm^{-1}; NMR δ 3.05 (s, 3 H), 4.47 (d, 1 H), 5.32 (d, 1 H), 6.6–7.1 (m, 14 H); UV λ_{EtOH} 284 nm (log ϵ 3.99), 277 (4.01), 270 (3.99), 257 (4.00); mass spectrum, *m/e* 328, 311, 222, 167, 165, 152, 134, 133, 132, 118, 92, 77. Anal. Calcd for $C_{22}H_{20}N_2O$: C, 80.30; H, 6.14; N, 8.53. Found: C, 80.30; H, 6.08; N, 8.33.

Acetylation of alcohol 5 (0.1 g) in pyridine–acetic anhydride (6:10) gave acetate 6: 71% yield (0.08 g); mp 165–166 °C; IR 1730, 1600, 1470, 1230, 1020, 920, 750, 710, 700 cm^{-1}; NMR δ 1.75 (s, 3 H), 3.32 (s, 3 H), 4.87 (d, 1 H), 6.31 (d, 1 H), 6.7–7.1 (m, 13 H), 7.4 (m, 1 H). Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.29; H, 5.91; N, 7.56. Acetate 6 (1.0 g) was hydrolyzed back to alcohol 5 (0.06 g) upon treatment with 10% methanolic potassium hydroxide.

Oxidation of Ketone 4 to 1-Methylbenzimidazole-2-carboxylic Acid. Ketone 4 (0.3 g) was dissolved in acetic acid (10 mL). A solution of *m*-chloroperbenzoic acid (0.48 g) in acetic acid (5 mL) was added. After 0.5 h at room temperature, 1-methylbenzimidazole-2-carboxylic acid precipitated out. It was collected and washed with chloroform. The product dissolves easily in water but not in $CHCl_3$: yield 0.35 g; mp 91–93 °C, with the loss of CO_2 (lit.[3,4,10] 90–93 °C dec); IR 3150–2700 (broad band), 1670, 1520, 1480, 1330, 1320, 845, 750 cm^{-1}; NMR (in D_2O) δ 3.45 (s, 3 H), 6.8–7.5 (m, 4 H). Acid 7 lost CO_2 on heating and gave 1-methylbenzimidazole which was identified by comparison with an authentic sample. The same effect was observed when the acid was allowed to stand at room temperature for 3 weeks. These findings confirm the observations of Tertov and Panchenko.[4] Moreover, the copper salt (complex?) of acid 7 was identical with the copper salt of 1-methylbenzimidazole-2-carboxylic acid prepared according to the method of Tertov and Koblik.[3]

The original acetic acid mother liquor was made basic with 10% sodium hydroxide and extracted four times with ether. Evaporation of ether gave benzophenone and 1-methylbenzimidazole which were identified by comparison with authentic samples.

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Registry No. 1c, 13436-48-1; 2c, 40110-18-7; 4, 57301-77-6; 5, 57301-81-2; 6, 73286-44-9; 8, 57301-63-0; diphenylketene, 525-06-4; diphenylacetylhydrazine, 6636-02-8; diphenylacetic acid, 117-34-0.

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Phosphindolin-3-one. A Useful Intermediate for Phosphindole Synthesis

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Phosphindole 1-oxide (1a) and phosphindoline 1-oxide (1b) are little-studied ring systems.[1] This is particularly surprising since 1c is isoelectronic with indole. Reported syntheses of this ring system have been plagued by ex-

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