Sulfoxonium Ylide Chemistry. VIII.[1] A Novel Rearrangement of Dimethylsulfoxonium Ylides

Junya Ide, Tetsuo Hiraoka, and Yukichi Kishida

Central Research Laboratories, Sankyo Co., Ltd., 1-2-58 Hiromachi, Shinagawa-ku, Tokyo 140

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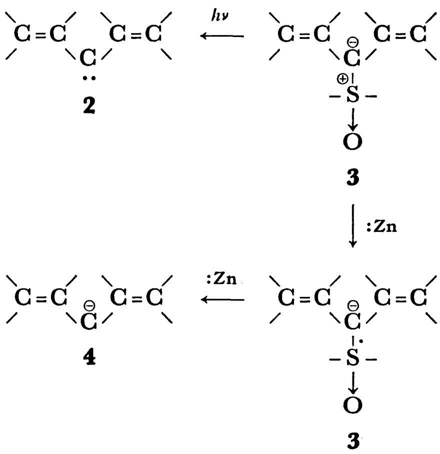
Reduction of dimethylsulfoxonium 3-ethoxycarbonyl-1-[1,2-bis(methoxycarbonyl)vinyl]-2-phenylallylide (**1**) and dimethylsulfoxonium 3-ethoxycarbonyl-1-[2-(ethoxycarbonyl)vinyl]-2-phenylallylide (**5**) with zinc in acetic acid gave (*Z*)- and (*E*)-3-methoxycarbonyl-4-ethoxycarbonyl-5-phenyl-3,5-hexadienoic acid methyl ester (**6a** and **6b**), and (*Z*)- and (*E*)-4-ethoxycarbonyl-5-phenyl-3,5-hexadienoic acid ethyl ester (**7a** and **7b**), respectively, whose structures were determined by the NMR spectral data and further chemical transformations. The reaction mechanism of the reductive rearrangement was proposed to proceed through an anion radical to form a four membered intermediate (**11**), which cleaved to non-conjugated dienes leading to *Z* and *E* conjugated products.

In the preceding paper,[1] we have reported that the reductive cleavage of sulfoxonium allylides with dissolving metal such as zinc in acetic acid proceeds through an anion radical produced by electron transfer from the metal surface to the sulfur atom of ylides followed by cleavage of carbon–sulfur bond to produce a carbanion. Furthermore, we reported on the photolysis of several dimethylsulfoxonium allylides,[2] in which the vinylallylide (**1**) afforded naphthalene derivatives supposedly produced through a carbene intermediate (**2**) followed by complex rearrangement.

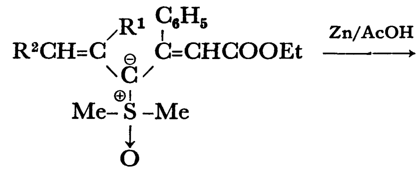
In the continuation of our studies on sulfoxonium ylides to clarify the chemical character of the carbon–sulfur ylide bond, it would be of interest to compare the chemical behavior of divinyl carbene (**2**) presumably generated by photolysis of the corresponding ylide (**3**) with divinyl carbanion (**4**) produced by dissolving metal reduction of **3**.



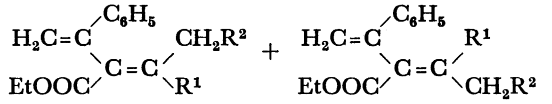
In the present paper we wish to describe a novel type of rearrangement of sulfoxonium vinylallylides *via* divinyl carbanion by dissolving metal reduction.

Results and Discussion

Treatment of dimethylsulfoxonium 3-ethoxycarbonyl-1-[1,2-bis(methoxycarbonyl)vinyl]-2-phenylallylide (**1**)[3] and dimethylsulfoxonium 3-ethoxycarbonyl-1-[2-(ethoxycarbonyl)vinyl]-2-phenylallylide (**5**)[3] with zinc in acetic acid at room temperature afforded a mixture of two geometrical isomers, (**6a** and **6b**) in 74% and (**7a** and **7b**) in 51% yield, respectively. The products obtained from **1** were successfully separated by silica gel column chromatography into **6a** and **6b** with a ratio of 88: 12 which was determined by the NMR spectroscopy. However, the separation of the mixture obtained from **5** was unsuccessful even by repeated column chromatography on silica gel or alumina. The ratio of two geometrical isomers (**7a** and **7b**) consisted of 40: 60 determined by the NMR spectroscopy.



1: $R^1=R^2=COOMe$
5: $R^1=H$, $R^2=COOEt$



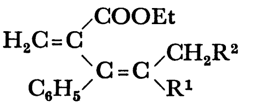
6a: $R^1=R^2=COOMe$ **6b**: $R^1=R^2=COOMe$
7a: $R^1=H$, $R^2=COOEt$ **7b**: $R^1=H$, $R^2=COOEt$

In the NMR spectra of **6a** and **6b**, terminal methylene protons were observed characteristically as AB quartet at δ 5.43 and 5.83 ppm (J=0.4 Hz), and δ 5.25 and 5.62 ppm (J=0.8 Hz), respectively. Likewise, terminal methylene protons of **7a** and **7b** appeared as AB quartet at δ 5.13 and 5.74 ppm (J=1.5 Hz), and δ 5.27 and 5.36 ppm (J=1.5 Hz), respectively. These terminal methylenes in **6a, b** and **7a, b** were chemically identified as 2,4-dinitrophenylhydrazone of formaldehyde liberated by ozonolysis.

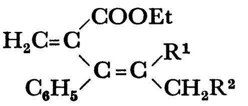
The methylene protons ($=C-\underline{CH_2}-COOMe$) of **6a** and **6b** appeared at δ 3.39 and 3.78 ppm as sharp singlet, respectively. The fact that the chemical shift of the methylene protons of **6b** appeared at lower field than that of **6a**, is apparently caused by anisotropic effects of the ethoxycarbonyl group at the β-position. Therefore, the geometry between the methoxycarbonylmethyl ($-CH_2COOMe$) and ethoxycarbonyl group in **6b** is assignable to *Z*-configuration, and in **6a** to *E*-configuration. The *E*-isomer (**6a**) is likely to be thermodynamically more stable than the *Z*-isomer (**6b**) because of less interraction between methoxycarbonyl methyl and ethoxycarbonyl group. This observation reflects the product distribution of **7**.

For **7a** the methylene ($-\underline{CH_2}COOEt$) and vinyl protons exhibited doublet at δ 3.19 ppm (J=7.5 Hz) and triplet at δ 7.1 ppm (J=7.5 Hz), respectively, and for **7b** doublet at δ 3.55 ppm (J=7 Hz) and triplet at δ 6.37 ppm (J=7 Hz), respectively. The chemical shifts of the vinyl proton of **7a** and the methylene protons ($=C-\underline{CH_2}-COOMe$) of **7b** appeared at lower field than those of **7b** and **7a**, respectively, due to the anisotropic effect of the ethoxycarbonyl group at the β-position. These observations indicate that the geometry between the methoxycarbonylmethyl ($-CH_2COOMe$) and ethoxycarbonyl group of **7a** is assigned to E-, and that of **7b** to Z-configuration.

Another possible structures (**6a′** and **6b′**) and (**7a′** and **7b′**) could be written for the reduction products obtained from sulfoxonium ylides (**1**) and (**5**), respectively. However, further chemical transformations and mechanistic consideration definitely excluded this possibility (*vide infra*).

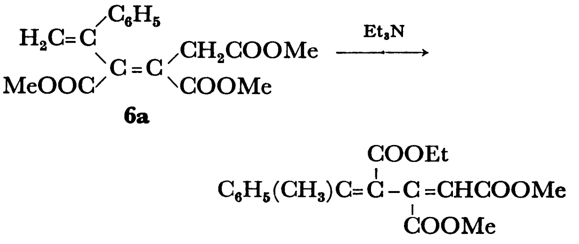


6a′: $R^1=R^2=COOMe$
7a′: $R^1=H$, $R^2=COOEt$

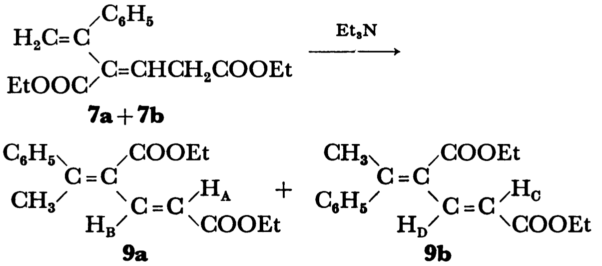


6b′: $R^1=R^2=COOMe$
7b′: $R^1=H$, $R^2=COOEt$

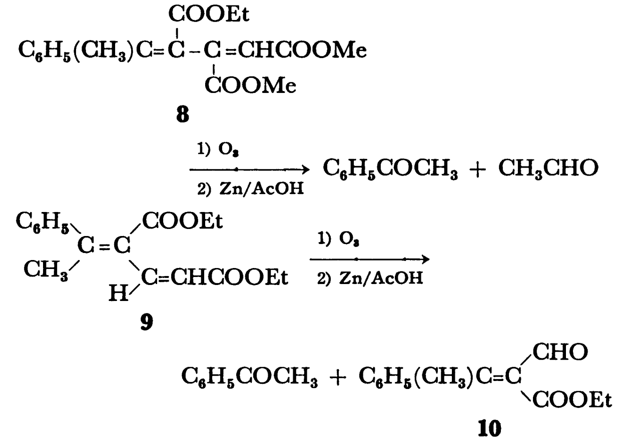
Treatment of the pure E-isomer (**6a**) with triethylamine in benzene furnished stereospecifically only one isomerized product (**8**), whose geometrical configuration was not clear. In its NMR spectrum, methyl and one vinyl protons appeared at δ 2.58 ppm (sharp singlet) and at δ 6.61 ppm (singlet), respectively, in addition to the peaks due to the two methoxycarbonyl and ethoxycarbonyl groups.

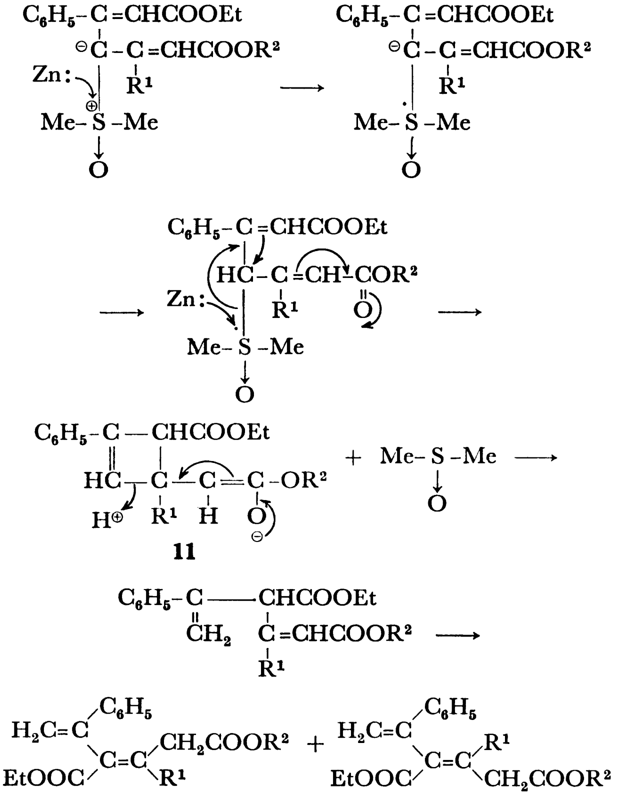


Analogously, base-catalysed isomerization of a mixture of **7a** and **7b** (36: 65) with triethylamine gave a mixture of two geometrical isomers (**9a**, and **9b**) in a ratio of 76: 24, which was determined by the NMR spectroscopy. In the NMR spectrum of **9a**, methyl protons appeared at δ 2.24 ppm as doublet (J=1 Hz), vinyl proton (H_A) at δ 5.88 ppm as doublet (J=16 Hz) and vinyl proton (H_B) at δ 7.30 ppm as quartet (J=16 and 1 Hz), and in that of **9b**, methyl protons appeared at δ 2.33 ppm as singlet, vinyl proton (H_C) at δ 6.07 ppm as doublet (J=16 Hz) and vinyl proton (H_D) at δ 7.76 ppm as doublet (J=16 Hz). The geometry of two vinyl protons in both **9a** and **9b** should be assigned to E-configuration from their coupling constant of J=16 Hz. The chemical shifts of the methyl (δ 2.33 ppm) and vinyl proton (H_D at δ 7.76 ppm) of **9b** appeared at lower field than that of **9a** (2.23 and 7.30 (H_B), respectively) due to the anisotropic effects of the ethoxycarbonyl and phenyl groups of **9b**. These facts indicate that the methyl group of **9b** preserves Z-configuration to the β-ethoxycarbonylgroup, and that of **9a** E-configuration.



Ozonolysis of **8** in dichloromethane followed by treatment with zinc liberated acetophenone, which was identified as 2,4-dinitrophenylhydrazone, together with acetaldehyde,[4] whereas a mixture of **9** (a mixture of Z





6: $R^1=COOMe$, $R_2=Me$; **7**: $R^1=H$, $R^2=Et$

and E (76 : 24)) by ozonolysis yielded acetophenone and 2-formyl-3-phenyl-2-butenoate (**10**), which was confirmed as 2,4-dinitrophenylhydrazone (mp 194—195 °C). Thus, other possible structures (**6a′**, **6b′**, **7a′**, and **7b′**) as reduction products from **1** and **5** were firmly excluded.

The reaction pathway for the present reductive cleavage of dimethylsulfoxonium vinylallylides is likely to proceed through an anion radical to form a four membered intermediate (**11**), which would be cleaved to an unstable non-conjugated diene leading finally to conjugated products. On these novel and complex reactions the proposed mechanism can only be viewed tentatively. The mechanistic investigation in detail is under continuation.

It seems to be quite interesting that divinyl carbanion and carbene system derived by dissolving metal reduction and photolysis from the corresponding sulfoxonium ylides, respectively, possess remarkably outstanding chemical bihavior, which are now under studying.

Experimental

All the melting points were uncorrected. NMR spectra were recorded on a Varian A-60 and HA-100 spectrometers using TMS as an internal standard, IR spectra were taken on a Hitachi EPI-G3 and UV spectra were obtained with Beckman DK-2 spectrophotometer.

Reduction of Dimethylsulfoxonium 3-Ethoxycarbonyl-1-[1,2-bis-(methoxycarbonyl)vinyl]-2-phenylallylide (1). To a solution of **1** (15.5 g, 38 mmol) in acetic acid (150 ml) was added zinc powder (25 g, 380 mmol) in many portions under controlling inner temperature at 18—20 °C with cold water, and the reaction mixture was stirred at room temperature for 10 h. The inorganic substrance was filtered and washed with ether. The filtrate was concentrated under reduced pressure. The residue was dissolved in ether (*ca.* 500 ml), and the ethereal solution was washed successively with 5% $NaHCO_3$ solution, water and saturated NaCl solution, and dried over anhydrous Na_2SO_4. After the evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel (80 g). Elution with hexane–benzene (3 : 1) gave 1.11 g (8.8% yield) of methyl (Z)-4-ethoxycarbonyl-3-methoxycarbonyl-5-phenyl-3,5-hexadienoate (**6b**), bp 140—143 °C/10^{-4} Torr (bath temp); IR (liquid): ν 1745, 1720, 1718, and 905 cm^{-1} ($=CH_2$); NMR ($CDCl_3$): δ 1.03 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.10 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 3.56 (3H, s; $COOCH_3$), 3.74 (3H, s; $COOCH_3$), 3.78 (2H, s; CH_2COOMe), 5.25 (1H, d, J=0.8 Hz; -CH), 5.62 (1H, d, J=0.8 Hz; =CH) and 7.4 ppm (5H, m; C_6H_5); Found: C, 65.21; H, 6.03%. Calcd for $C_{18}H_{20}O_6$: C, 65.02; H, 6.07%. Elution with hexane–benzene (1 : 1—1 : 3) afforded 7.99 g (63.3% yield) of methyl (E)-3-ethoxycarbonyl-4-methoxycarbonyl-5-phenyl-3,5-hexadienoate (**6a**), bp 140—141 °C/10^{-4} Torr (bath temp); IR (Liquid): ν1745, 1720, 1705, and 905 cm^{-1} ($=CH_2$); NMR ($CDCl_3$): δ 1.18 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.22 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 3.60 (3H, s; $COOCH_3$), 3.81 (3H, s; $COOCH_3$), 5.43 (1H, d, J=0.4 Hz; -CH), 5.83 (1H, d, J=0.4 Hz; =CH) and 7.4 ppm (5H, m; C_6H_5); Found: C, 64.78; H, 6.11%. Calcd for $C_{18}H_{20}O_6$: C, 65.02; H, 6.07%.

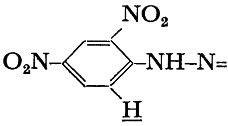
Reduction of Dimethylsulfoxonium 3-Ethoxycarbonyl-1-[2-(ethoxycarbonyl)vinyl]-2-phenylallylide (5). To a solution of **5** (8.4 g, 23 mmol) in acetic acid (100 ml) was added zinc powder (15 g, 230 mmol) in many portions under controlling inner temperature at 18—20 °C with cold water, and the reaction mixture was stirred over night (13 h). The inorganic substance was filtered and washed with ether. The filtrate was concentrated under reduced pressure. The residue was dissolved in ether (*ca.* 300 ml), and the ethereal solution was washed successively with 5% $NaHCO_3$ solution, water, and saturated NaCl solution, and dried over anhydrous Na_2SO_4. After the evaporation of the solvent under reduced pressure, the residue was distilled *in vacuo* to give 3.4 g (51.2% yield) of a mixture of ethyl (Z)- and (E)-4-ethoxycarbonyl-5-phenyl-3,5-hexadienoate (**7a** and **7b**) in a ratio of 40 : 60, bp 120—121 °C/10^{-4} Torr; IR (Liquid): ν 1745, 1720, and 903 cm^{-1} ($=CH_2$); UV (EtOH): λ_{max} 238 nm (ε 12440); NMR (100 Mc, $CDCl_3$): For Z-isomer (7a): δ 1.10 and 1.23 (6H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.08 and 4.21 (4H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 3.19 (2H, d, J=7.5 Hz; $=C\text{–}C\underline{H}_2COOEt$), 7.10 (1H, t, J=7.5 Hz; $=C\underline{H}\text{–}CH_2\text{–}$), 5.13 (1H, d, J=1.5 Hz; =CH), 5.74 (1H, d, J=1.5 Hz; =CH), and 7.25 ppm (5H, s; C_6H_5); For E-isomer (**7b**): δ 1.01 and 1.27 (6H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.12 and 4.17 (4H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 3.55 (2H, d, J=7 Hz; $=C\text{–}CH_2COOEt$), 6.37 (1H, t, J=7 Hz; $=C\underline{H}\text{–}CH_2$), 5.27 (1H, d, J=1.5 Hz; =CH), 5.36 (1H, d, J=1.5 Hz; =CH), and 7.25 ppm (5H, s; C_6H_5); Found: C, 70.69; H, 7.15%. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%.

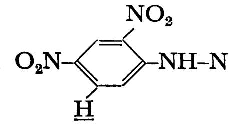
Ozonolysis of a Mixture of Methyl(Z)- *and* (E)-*4-Ethoxycarbonyl-3-methoxycarbonyl-5-phenyl-3,5-hexadienoate (6a and 6b).* Into a solution of **6** (a mixture of **6a** and **6b** (88 : 12)) (1.5 g, 4.5 mmol) in acetic acid (50 ml) containing small amount of KI freshly generated ozone was passed under cooling at 15—18 °C with cold water until iodine deposited. To the reaction mixture was added zinc (1 g) and water (20 ml), and stirred at room temperature for 2 h. The reaction mixture was submitted to steam-distillation, and the distilate was passed into a saturated solution of 2,4-dinitrophenylhydrazine in 2 M-HCl (150 ml). Deposited yellow precipitate was collected by filtration, and recrystallized from ethyl acetate to give 250 mg (26.5% yield) of 2,4-dinitrophenylhydrazone of formaldehyde, mp 162—163 °C, which was identified with an authentic sample in the mixed melting point and in their IR spectra.

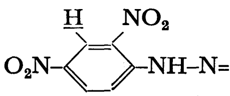
Ozonolysis of a Mixture of Ethyl (Z)- *and* (E)-*4-Ethoxycarbonyl-5-phenyl-3,5-hexadienoate (7a and 7b).* Into a solution of **7** (a mixture of **7a** and **7b** (40 : 60)) (1 g, 3.46 mmol) in acetic acid (40 ml) containing small amount of KI, freshly generated ozone was passed under cooling at 15—18 °C with cold water until iodine deposited. The same work-up as described above afforded 240 mg (33% yield) of 2,4-dinitrophenylhydrazone of formaldehyde, mp 162—163 °C.

Isomerization of Methyl (E)*4-Ethoxycarbonyl-3-methoxycarbonyl-5-phenyl-3,5-hexadienoate (6a) to Methyl 4-Ethoxycarbonyl-3-methoxycarbonyl-5-phenyl-2,4-hexadienoate (8).* A solution of **6a** (3.0 g, 9 mmol) and triethylamine (9 ml) in benzene (75 ml) was heated under reflux for 30 h. After the evaporation of the solvent, the residue was chromatographed on silica gel (100 g). Elution with benzene afforded 1.15 g (38.3% yield) of **8**, bp 142—143 °C/10^{-4} Torr (bath temp); IR (Liquid): ν 1720, 1718, and 1715 cm^{-1}; NMR ($CDCl_3$): δ 1.24 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.22 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 2.58 (3H, s; $=CCH_3$), 3.60 (3H, s; $COOCH_3$), 3.69 (3H, s, $COOCH_3$), 6.61 (1H, s; =CH), and 7.25 (5H, m; C_6H_5); Found: C, 64.78; H, 6.26%. Calcd for $C_{18}H_{20}O_6$: C, 65.02; H, 6.07%. Further elution with benzene–ethyl acetate (3 : 1) gave a mixture of **6a** and **8** (1.12 g).

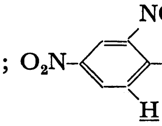
Isomerization of a Mixture of Ethyl (Z)- *and* (E)-*4-Ethoxycarbonyl-5-phenyl-3,5-hexadienoate (7a and 7b) to a Mixture of Ethyl* (Z)- *and* (E)-*4-Ethoxycarbonyl-5-phenyl-2,4-hexadienoate (9a and 9b).* A solution of **7** (a mixture of **7a** and **7b** (40 : 60)) (1.6 g, 5.5 mmol) and triethylamine (5 g, 50 mmol) in benzene (25 ml) was heated under reflux for 2 h. After the evaporation of the solvent, the residue was distilled *in vacuo* to give 1.2 g (75% yield) of a mixture of **9a** and **9b**, bp 140—141 °C/10^{-4} Torr; IR (liquid): ν 1720, 1718 cm^{-1}; NMR ($CDCl_3$): For *E*-isomer (**9a**): δ 1.22 and 1.38 (6H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.14 and 4.40 (4H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 2.24 (3H, s; CH_3), 5.88 (1H, d, J=16 Hz; =CHCOOEt), 7.30 (1H, d, J=16 Hz; =CH), and 7.35 ppm (5H, m; C_6H_5); For *Z*-isomer (**9b**): δ 0.87 and 1.30 (6H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 3.94 and 4.27 (4H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 2.33 (3H, s; CH_3), 6.07 (1H, d, J=16 Hz; =CHCOOEt), 7.76 (1H, d, J=16 Hz; =CH), and 7.25 ppm (5H, m; C_6H_5); UV (EtOH) λ_{max} 234 (ε 11160), and 285 nm (ε 14660); Found: C, 70.86; H, 7.02%. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%.

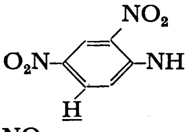
Ozonolysis of Methyl 4-Ethoxycarbonyl-3-methoxycarbonyl-5-phenyl-2,4-hexadienoate (8). Into a solution of **8** (800 mg, 2.4 mmol) in dichloromethane (12 ml) was passed freshly generated ozone (250 mg, 5.2 mmol) at −50 °C. To the reaction mixture was added zinc powder (800 mg), acetic acid (0.4 ml) and water (0.2 ml), and stirred at room temperature for 2 h. After filtration of the inorganic substance, the filtrate was concentrated under reduced pressure. To the residue was added a solution of 2,4-dinitrophenylhydrazine (2.4 g in H_2SO_4 (12 ml), H_2O (18 ml) and EtOH (150 ml)), and heated under reflux for 30 min. After addition of water (200 ml) and extraction with ethyl acetate, the organic layer was washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel (30 g). Elution with benzene gave 2,4-dinitrophenylhydrazone of acetophenone (110 mg, 15.2% yield), mp 253—255 °C, which showed no depression in mixed melting point with an authentic specimen. Further elution with benzene gave 2,4-dinitrophenylhydrazone of acetaldehyde (400 mg, 74% yield),[4] mp 159—161 °C (from EtOH), which showed no depression in mixed melting point with an authentic samples; NMR ($CDCl_3$): δ 2.16 (3H, d, J=6 Hz; $N=CH-C\underline{H}_3$), 7.69 (1H, q, J=6 Hz; $N=CH-CH_3$), 8.01 (1H, d, J=10 Hz; 

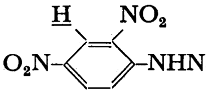
), 8.40 (1H, dd, J=2.5 and J=10 Hz; 

), 9.19 (1H, d, J=2.5 Hz: 

), and 11.16 (1H, m, NH); Found: C, 42.62; H, 3.70; N, 24.89%. Calcd for $C_8H_8N_4O_4$: C, 42.86; H, 3.59; N 24.99%.

*Ozonolysis of a Mixture of Ethyl (*Z*)- and (*E*)-4-Ethoxycarbonyl-5-phenyl-2,4-hexadienoate (9a and 9b).* Into a solution of **9** (a mixture of **9a** and **9b** (76: 24)) (1.0 g, 3.5 mmol) in dichloromethane (55 ml) was passed freshly generated ozone (*ca.* 8 mmol) at −50 °C. To the reaction mixture was added zinc powder (840 mg, 14 mmol), acetic acid (0.5 ml) and water (0.1 ml), and stirred at room temperature for 2 h. After the same procedure as described above, the crude hydrazone was chromatographed on silica gel (30 g). Elution with benzene gave 36 mg of 2,4-dinitrophenylhydrazone of acetophenone, mp 253—255 °C (from EtOH), which showed no depression with an authentic sample in mixed melting point; Further elution with benzene gave 148 mg (10.7% yield) of orange crystals of 2,4-dinitrophenylhydrazone of ethyl 2-formyl-3-phenyl-2-butenoate (**10**), mp 194—195 °C (decomp) (from ethyl acetate): NMR ($CDCl_3$): δ 1.48 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.50 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 2.30 (3H, s; $=CCH_3$), 7.42 (5H, m; C_6H_5), 7.69 (1H, s; =CH–), 7.80 (1H, d, J=9 Hz; 

), 8.32 (1H, dd, J=9 and J=3 Hz; 

), 9.07 (1H, d, J=3 Hz; 

), and 10.98 ppm (1H, m; NH); Found: C, 57.64; H, 4.53; N, 13.93%. Calcd for $C_{19}H_{18}N_4O_6$: C, 57.28; H, 4.55; N, 14.07%.

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References

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4) In addition to acetophenone, a significant amount of acetaldehyde was obtained (see Experimental), which was presumably produced by phenyl migration on the decomposition of the ozonide of **9** with zinc in acidic conditions.