Sulfoxonium Ylide Chemistry. VII.[1] Reductive Cleavage of Dimethylsulfoxonium Allylides

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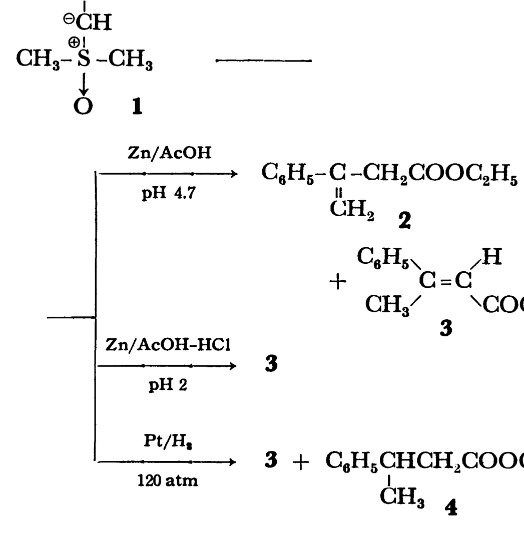
Reductive cleavage of dimethylsulfoxonium allylides with zinc in acetic acid or by hydrogenation over platinum at high pressure (120 atm) has been investigated. Reduction of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (**1**) with zinc gave predominantly ethyl 3-phenyl-3-butenoate (**2**) together with ethyl (*E*)-3-phenyl-2-butenoate (**3**) (90: 10). However, under the more acidic conditions (pH 2), **3** was the exclusive product. Hydrogenation of **1** over platinum afforded a mixture of **3** and ethyl 3-phenylbutanoate (**4**). Reduction of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenyl-1-(phenylcarbamoyl)allylide (**6**) either with zinc or by hydrogenation gave ethyl (*Z*)-3-phenyl-4-phenylcarbamoyl-2-butenoate (**7**). Hydrogenation of dimethylsulfoxonium 1-benzoyl-3-ethoxycarbonyl-2-phenylallylide (**9**) at room temperature provided ethyl (*Z*)-3,5-diphenyl-5-oxo-2-pentenoate (**10**) and 4,6-diphenyl-2-pyrone (**11**), and at 80 °C **11** and ethyl 3,5-diphenyl-5-oxopentanoate (**12**).

In the continuation of our studies on sulfoxonium ylides to clarify the chemical behavior of carbon–sulfur ylide bond, the reduction of sulfoxonium ylides by a dissolving metal or catalytic hydrogenation is of interest from a synthetic view point. It is already known that desulfurizations of allyl sulfide and thioacetals are effected by dissolving metal such as Raney-Ni or sodium. Additionally, dissolving metal reduction either in the presence of a proton donor or followed by treatment with a proton donor offers the advantage of selectivity in reduction or of stereoselectivity. There has been, however, only one report on the reduction of a sulfoxonium ylide reported by Corey and Chaykovsky.[2]

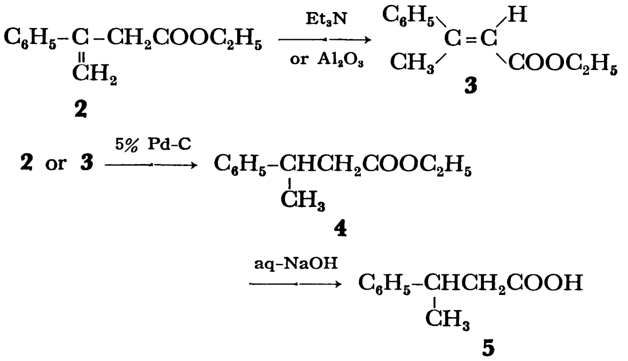
In the present paper, we would like to describe the reduction of sulfoxonium allylides with zinc in acetic acid and by catalytic reduction over platinum in acetic acid at high pressure, along with certain mechanistic aspects of these processes.

Results and Discussion

Treatment of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (**1**) with zinc powder in acetic acid (pH 4.7) at 16—18 °C under an argon atmosphere gave ethyl 3-phenyl-3-butenoate (**2**) and ethyl (*E*)-3-phenyl-2-butenoate (**3**) in a ratio of 90: 10 (by GLC analysis) in 92% yield. On the contrary, under more acidic conditions using a small amount of hydrochloric acid (pH 2), **1** afforded **3** exclusively. Reduction of **1** over platinum in acetic acid at 120 atm of hydrogen at room temperature gave a mixture of **3** and ethyl 3-phenylbutanoate (**4**) in 88% yield. However, under atmospheric pressure the reduction was not effected and the starting material (**1**) was recovered.



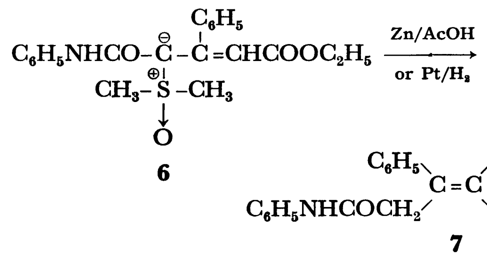
Base-catalysed isomerization of **2** was readily effected with alumina or triethylamine to give the more stable isomer (**3**). Catalytic hydrogenation of **2** or **3** over 5% palladium–charcoal afforded **4**, which was hydrolysed to the corresponding acid (**5**).



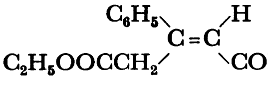
The NMR, UV, and IR spectral data of **2**, **3**, and **4** also support their structures. Terminal methylene protons of **2** appeared at δ 5.21 and 5.48 ppm (J=1.2 Hz). The UV spectrum of **2** showed λ_{max} (EtOH) 243 nm (ε 10600), which was very similar to that of α-methylstyrene (λ_{max} (EtOH) 240 nm (ε 12000)),[3] and its IR spectrum exhibited a band at 909 cm^{-1} characteristic of terminal methylene group. The *E*-configuration was assigned to **3** based on the UV spectrum showing its absorption maximum at 265 nm (ε 15860).[4] From a synthetic view point this method seems to be preferable for the preparation of the unconjugated ester (**2**) which is hardly accessible because of its chemical instability.

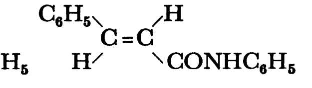
Reduction of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenyl-1-(phenylcarbamoyl)allylide (**6**) either with zinc in acetic acid or over platinum in acetic acid under

120 atm of hydrogen at room temperature afforded ethyl β-(phenylcarbamoylmethyl)cinnamate (**7**), mp 169—170 °C, in 66% and 73% yield, respectively.



In the NMR spectrum of **7**, methylene and vinyl protons appeared as singlets at δ 4.16 and 6.57 ppm, respectively. The UV spectrum of **7** showed λ_{max} (EtOH) 224 (ε 13880), 247 (ε 22200), and 270 nm (ε 15850) which was similar to the additive chromophore of ethyl (*E*)-phenyl-2-butenoate (**3**) and acetanilide (λ_{max} (EtOH) 242 nm (ε 13200)),[5] whereas the UV spectrum of *trans*-cinnamanilide (**8**) showed λ_{max} (EtOH) 221 (ε 18600), 240 (ε 4800), and 295 nm (ε 25800),[6] which would be appropriate for that of the other double bond isomer (**7′**).


7′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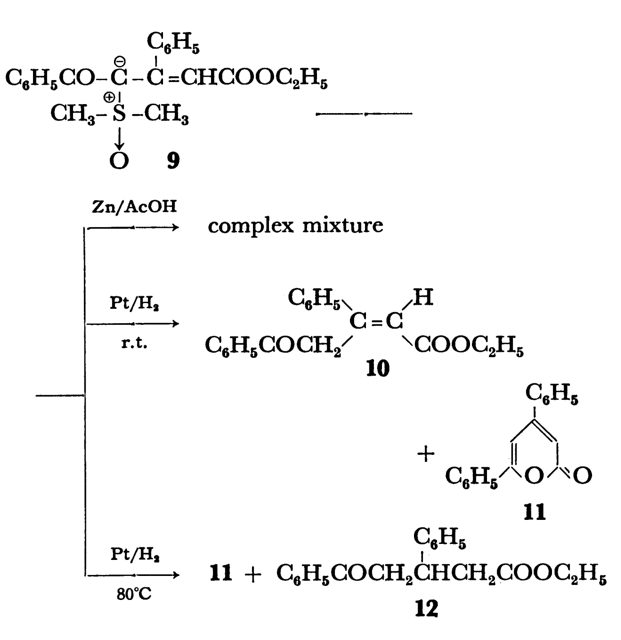
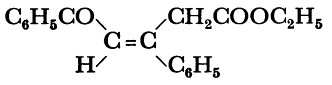
Treatment of dimethylsulfoxonium 1-benzoyl-3-ethoxycarbonyl-2-phenylallylide (**9**) with zinc in acetic acid at 16—18 °C resulted in a complex mixture, whereas its reduction over platinum in acetic acid under 120 atm at room temperature afforded ethyl (*Z*)-β-(benzoylmethyl)cinnamate (**10**), mp 85—86 °C and 4,6-diphenyl-2-pyrone (**11**), mp 136—137 °C (lit, mp 142 °C)[7] in 20 and 13% yield, respectively. However, in the reduction of **9** at 80 °C, the pyrone (**11**) and ethyl 3,5-diphenyl-5-oxobutanoate (**12**), mp 61—62 °C, were obtained in 60 and 9% yield, respectively.



The assignment of the position of the double bond and *Z*-configuration to **10** was based on the NMR and UV spectral data. In the NMR spectrum of **10** methylene and vinyl protons appeared at δ 4.87 (singlet) and 6.40 ppm (singlet), respectively. Its UV spectrum showed λ_{max} (EtOH) 246 (ε 21750) and 268 nm (ε 16630), which is in good agreement with the chromophore bearing acetophenone (λ_{max} (EtOH) 243 nm (ε 13200)[8]) and ethyl (*E*)-3-phenyl-2-butenoate (**3**). Another possible structure (**13**) which should have a similar chromophore with (*E*)-1,3-diphenyl-2-buten-1-one (**14**) (λ_{max} (EtOH) 227.5 (ε 9600), 262.5 (ε 10500) (sh), and 295 nm (ε 16000)),[9] can be excluded by comparing with that of **10**. Its IR spectrum revealed the carbonyl band at 1715 cm^{-1} which is appropriate for an α,β-unsaturated ester, but not for an α,β-unsaturated benzoyl group.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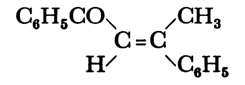
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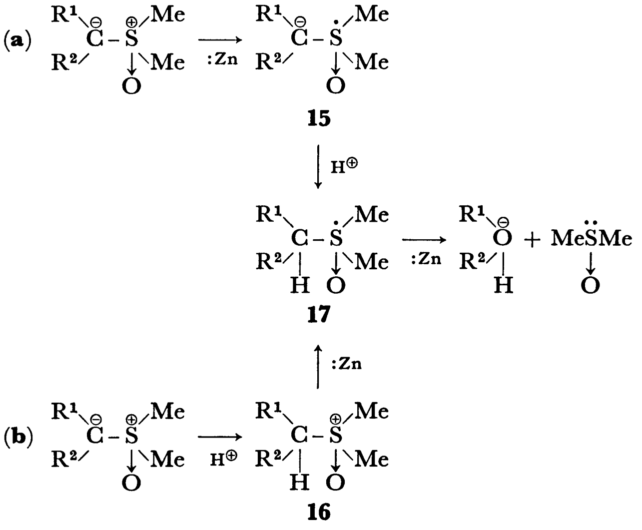
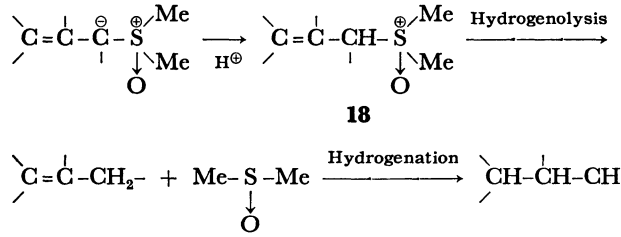
The NMR spectrum of **11** showed two vinyl protons as AB quartet with a small coupling constant at δ 6.48 and 6.98 ppm (J=1.3 Hz) and its UV spectrum exhibited λ_{max} (EtOH) 229 (ε 10880), 236 (ε 11200), 262 (ε 23100), and 344 nm (ε 10200).[10] The pyrone (**11**) was directly compared with an authentic sample prepared according to the method of Schulte *et al.*[7] The structure of **12** was determined by the examination of its UV and NMR spectra (see Experimental) and elemental analysis. The UV spectrum of **12** showed λ_{max} (EtOH) 243 nm (ε 12930), which was very close to that of acetophenone (*vide supra*),[8] supporting the existence of $C_6H_5COCH_2$ moiety.

Reduction of a sulfoxonium ylide with zinc in acetic acid could be well interpreted as proceeding through an anion radical (**15**) produced by electron transfer from the metal surface to sulfur of ylide (type "**a**"), or radical (**17**) produced by electron transfer to the sulfoxonium ion (**16**) fromed by protonation to ylide in acidic conditions (type "**b**").[11] A further electron transfer to the resulting radical (**17**) leads to the cleavage of carbon–sulfur bond. This reductive cleavage reaction

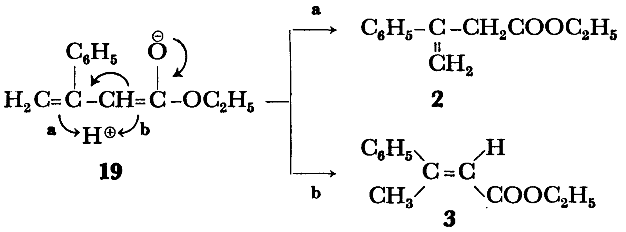


of type "**b**" by dissolving metal has been found in ammonium, sulfonium, and phosphonium salts.[11)]

On the other hand, the sulfoxonium allylide over platinum in acidic medium at high pressure of hydrogen is likely to undergo hydrogenolysis of allylsulfoxonium salt (**18**) produced by protonation to the ylide, and the resulting allyl group could be further hydrogenated partially to the saturated product depending upon the reaction conditions and/or the character of the substituents on the double bond.



It is noteworthy that in the reduction of **1** with zinc the non-conjugated ester (**2**) and the conjugated ester (**3**) are obtained selectively depending on the acidity of reaction medium. This would be attributed to the mode of protonation of the plausible reaction intermediate (**19**), in which weak acids lead to the kinetically-controlled product (**2**) by proton attack at the central position of the enolate anion, and strong acids or equilibrating conditions give the thermodynamically-controlled one (**3**) by attack of the proton at the terminal position according to the Ingold's theory.[12)]

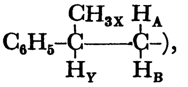


Experimental

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-2-phenylallylide (1) with Zinc in Acetic Acid. *a) At pH 4.7*: To a solution of **1** (15 g, 57 mmol) in glacial acetic acid (160 ml) was added zinc powder (39 g, 570 mmol) in many portions so as to control the inner temperature at 16—18 °C with external cooling, and the reaction mixture was stirred at room temperature for 8 h. The inorganic substances were filtered and washed with ether. The filtrate was concentrated under reduced pressure. The residue was dissolved in ether (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 (220 g). Elution with hexane–benzene (5: 1) gave ethyl (*E*)-3-phenyl-2-butenoate (**3**) (990 mg; 9.2% yield), bp 105—106 °C/1 Torr; IR (Liquid): ν 1710, 1625, and 1170 cm^{-1}; NMR ($CDCl_3$): δ 1.15 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.05 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 2.54 (3H, d, J=1.2 Hz; =C–CH_3), 6.07 (1H, q, J=1.2 Hz; =C–H), 7.3 ppm (5H, m; C_6H_5–); UV (EtOH): λ_{max} 265 nm (ε 15860); Found: C, 75.84; H, 7.54%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. Elution with hexane–benzene (3: 1) gave ethyl 3-phenyl-3-butenoate (**2**) (9.84 g, 90.8% yield), bp 98—100 °C/1 Torr; IR (Liquid): ν 1735 (–$COOC_2H_5$) and 909 cm^{-1} (=CH_2); NMR ($CDCl_3$): δ 1.15 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.08 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 3.41 (3H, d, J_{AX}=1.2 Hz, =C–$C\underline{H}_{2X}$–$COOC_2H_5$), 5.21 (1H, q, J_{AB}=J_{AX}=1.2 Hz; =C–H_A (*trans* to phenyl group)), 5.48 (1H, d, J_{AB}=1.2 Hz; =C–H_B (*cis* to phenyl group)), and 7.3 ppm (5H, m; C_6H_5); UV (EtOH): λ_{max} 243 nm (ε 10600); Found: C, 75.60; H, 7.55%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

b) At pH 2 Containing Hydrogenchloride: The Ylide (**1**) (5 g, 19 mmol) was dissolved in glacial acetic acid (70 ml), and pH value was adjusted at 1.8—2.0 by adding small amount of concd HCl (*ca.* 2 ml). To the solution was added zinc powder (13 g, 200 mmol) in many portions so as to control the inner temperature at 16—18 °C with external cooling and the reaction mixture was stirred at room temperature for 8 h. After the same work-up as described in **a**), the residue was distilled *in vacuo* to give **3**, bp 105—106 °C/1 Torr (3.2 g, 90% yield).

Catalytic Hydrogenolysis of Dimethylsulfoxonium 3-Ethoxycarbonyl-2-phenylallylide (1) over Platinum in Acetic Acid. A solution of **1** (8.8 g, 33 mmol) in glacial acetic acid (60 ml) was hydrogenated over PtO_2 (1.8 g) in an autoclave at 120 atm of hydrogen at room temperature for 10 h. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (140 g). Elution with hexane–benzene (5: 1) afforded **3** (4.04 g, 64.4% yield) and elution with hexane–benzene (3: 1) gave ethyl 3-phenylbutanoate (**4**) (1.52 g, 24% yield), bp 95—97 °C/2 Torr; IR (Liquid): ν 1735 cm^{-1} ($COOC_2H_5$); NMR ($CDCl_3$): δ 1.14 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.06 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 1.3 (3H, d, J=7 Hz; H_X in  $C_6H_5\text{–}\overset{CH_{3X}}{\underset{H_Y}{C}}\text{——}\overset{H_A}{\underset{H_B}{C}}\text{–}$), 2.41 (1H, dd, J_{AY}=2 Hz, J_{AB}=15.5 Hz; H_A), 2.71 (1H, d, J_{AB}=15.5 Hz; H_B), 3.30 (1H, dq, J_{AY}=2 Hz, J_{XY}=7 Hz; H_Y), 7.25 ppm (5H, m; $C_6\underline{H}_5$); Found: C, 75.41; H, 8.32%. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39%.

*Isomerization of Ethyl 3-Phenyl-3-butenoate (2) to Ethyl (*E*)-3-Phenyl-2-butenoate (3).* *a) With Alumina*: A solution of **2** (2.5 g) in hexane (10 ml) was placed on Al_2O_3 (Woelm grade I) (50 g) and eluted with hexane–benzene (1: 1) to give 2.3 g of **3**.

b) With Triethylamine: A solution of **2** (2.5 g) and triethylamine (500 mg) in benzene (10 ml) was heated under reflux for 1 h. After evaporation under reduced pressure, the residue was distilled *in vacuo* to give 2.2 g of **3**, bp 105—106 °C/1 Torr.

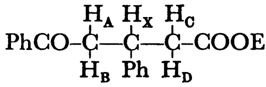
*Hydrogenation of Ethyl 3-Phenyl-3-butenoate (2) or Ethyl (*E*)-3-Phenyl-2-butenoate (3).* A solution of **2** or **3** (1.4 g) and Pd-charcoal (5%) (500 mg) in ethyl acetate (10 ml) was hydrogenated in hydrogen atmosphere under ordinary pressure. After removal of the catalyst, the solution was concentrated under reduced pressure. The residue was distilled *in vacuo* to afford **4**, bp 95—97 °C/2 Torr.

Hydrolysis of Ethyl 3-Phenylbutanoate (4). The ester (**4**) (1.2 g) was dissolved in ethanol (10 ml) and 10% NaOH (6 ml), and the solution was heated at 50 °C for 3 h. The reaction mixture was neutralized with acetic acid and concentrated under reduced pressure. After the addition of water (10 ml) and extraction with ethyl acetate, the organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was distilled *in vacuo* to give 850 mg of the corresponding acid (**5**), bp 132—136 °C/2 Torr (bath temp); Found: C, 73.45; H, 7.41%. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.36%.

Reduction of Dimethylsulfoxonium 3-Ethoxycarbonyl-2-phenyl-1-(phenylcarbamoyl)allylide (6) with Zinc in Acetic Acid. To a solution of **6** (15.6 mmol, 6 g) in glacial acetic acid (60 ml) was added zinc powder (10 g, 160 mmol) in many portions so as to control the inner temperature at 16—18 °C with external cooling. The reaction mixture was stirred at room temperature for 15 h. The inorganic substances were filtered and washed with CH_2Cl_2 (100 ml). The filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform (400 ml), and the solution was washed successively with 5% $NaHCO_3$ solution, water and saturated NaCl solution, and dried over Na_2SO_4. After the evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel (50 g). Elution with benzene gave ethyl β-(phenylcarbamoylmethyl)cinnamate (**7**; 3.18 g, 66% yield), mp 169—170 °C (from EtOH); IR (Nujol): ν 3100—3300 (NH), 1700, 1650, 1620, and 1600 cm^{-1} (CONH, $=CCOOC_2H_5$); NMR ($CDCl_3$): δ 1.37 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.41 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 4.15 (2H, s; $COC\underline{H}_2C=$), 6.56 (1H, s; =CH–), and 7.65 ppm (10H, m; C_6H_5); UV (EtOH): λ_{max} 224 (ε 13880), 247 (ε 22200), and 270 nm (ε 15850) (shoulder); Found: C, 73.48; H, 6.18; N, 4.53%. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53%.

Catalytic Hydrogenolysis of Dimethylsulfoxonium 3-Ethoxycarbonyl-2-(phenylcarbamoyl)allylide (6) over Platinum in Acetic Acid. A solution of **6** (2.1 g, 5.4 mmol) and PtO_2 (500 mg) in glacial acetic acid (20 ml) was hydrogenated in an autoclave at 125 atm of hydrogen at room temperature for 12 h. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (20 g). Elution with benzene gave **7** (1.22 g, 73% yield), mp 169—170 °C (from EtOH).

Catalytic Hydrogenolysis of Dimethylsulfoxonium 1-Benzoyl-3-ethoxycarbonyl-2-phenylallylide (9). *a) At Room Temperature*: A solution of **9** (4 g, 11 mmol) in glacial acetic acid (45 ml) was hydrogenated over PtO_2 (800 mg) in an autoclave at 125 atm of hydrogen at room temperature for 10 h. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (70 g). Elution with hexane–benzene (2: 1) gave ethyl (Z)-β-(benzoylmethyl)cinnamate (**10**, 0.64 g, 20.2% yield), mp 85—86 °C (colorless needles, from EtOH); IR (Nujol): ν 1715 cm^{-1} ($C_6H_5C=CHCOOC_2H_5$); NMR ($CDCl_3$) δ 1.26 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.18 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 4.87 (2H, s; $COCH_2C=$), 6.40 (1H, s; =CH–), 7.4 (8H, m; aromatic protons), and 8.1 ppm (2H, m; aromatic protons); UV (EtOH): λ_{max} 246 (ε 21750), and 268 nm (ε 16630); Found: C, 77.21; H, 7.21%. Calcd for $C_{19}H_{18}O_3$: C, 77.52; H, 7.16%. Elution with hexane–benzene (1: 1) afforded 4,6-diphenyl-2-pyrone (**11**, 350 mg, 13% yield), mp 137—138 °C (lit, mp 142 °C;[7] 138—139 °C;[10b]) IR (Nujol): ν 1702 cm^{-1} (pyrone CO); NMR ($CDCl_3$): δ 6.47 (1H, d, J=1.5 Hz; =CH), 6.97 (1H, d, J=1.5 Hz; =CH), and 7.4—8.0 ppm (10H, m); UV (EtOH): λ_{max} 229 (ε 10880), 236 (ε 11200), 262 (ε 23100), and 344 nm (ε 10200); Found: C, 82.17; H, 4.80%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%. The mixed melting point of **11** with the authentic sample prepared by the method[7] showed no depression.

b) At 80 °C: A solution of **9** (7.1 g 19.2 mmol) in glacial acetic acid (50 ml) was hydrogenated over PtO_2 (1.2 g) in an autoclave at 125 atm of hydrogen at 80 °C for 10 h. The catalyst was removed by filtration and the solvent was concentrated under reduced pressure. The residue was chromatographed on silica gel (120 g). Elution with hexane–benzene (3: 1) gave ethyl 3,5-diphenyl-5-oxobutanoate (**12**, 500 mg, 8.8% yield), mp 61—62 °C (colorless crystals, from hexane–EtOH): IR (Nujol): ν 1745 ($COOC_2H_5$) and 1680 cm^{-1} (CO); NMR (100 Mc. $CDCl_3$); for  $PhCO\text{-}\overset{H_A}{\underset{H_B}{C}}—\overset{H_X}{\underset{Ph}{C}}—\overset{H_C}{\underset{H_D}{C}}\text{-}COOEt$: δ 1.10 (3H, t, J=7 Hz; $COOCH_2C\underline{H}_3$), 4.0 (2H, q, J=7 Hz; $COOC\underline{H}_2CH_3$), 2.80 (H_C, q, J_{CD}=15 Hz, J_{CX}=7 Hz), 2.61 (H_D, q, J_{CD}=15 Hz, J_{DX}=8 Hz), 3.39 (H_A, q, J_{AB}=15 Hz, J_{AX}=6.5 Hz), 3.24 (H_B, q, J_{AB}=15 Hz, J_{BX}=8 Hz), 3.86 (H_X, m: about 9 lines containing splittings matching J_{AX}, J_{BX}, J_{CX}, and J_{DX}), 7.22 (5H, s; C_6H_5), and 7.9 and 7.5 ppm (5H, m: C_6H_5CO); UV (EtOH): λ_{max} 243 nm (ε 12930); Found: C, 77.46; H, 6.66%. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80%.

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