Reaction of Silyl Enol Ethers with Arenediazonium Salts. Part 2. α-Amination of Esters

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Diazonium salts efficiently serve as electrophilic aminating reagents of esters. The reaction of arenediazonium tetrafluoroborates with ketene silyl ketals yielded α-azo or α-hydrazono esters in good to excellent yields under very mild conditions. Hydrogenation of those esters gave α-amino esters quantitatively.

We have studied various synthetic routes to α-amino acid precursors (mainly α-keto acids); the reactions investigated so far are double carbonylation[1] and reductive double carbonylation[2] of organic halides, oxidation of α-hydroxy esters or cyanohydrins,[3] cyanation of carboxylic acid halides,[4] carbonylative cyanation of organic halides[5] and amido carbonylation.[6] A further important method for synthesizing α-amino acids is by α-amination of carboxylic acid derivatives. A conventional and relatively easy approach to this is the reaction of α-halogeno or α-hydroxy carboxylic acid derivatives with ammonia or amines (route a, Scheme 1). On the other hand, a less developed and challenging approach is the reaction of carboxylic acid enolates or their derivatives with electrophilic aminating reagents (route b). Owing to the increasing utilization of strong bases like lithium diisopropylamide (LDA) in recent organic syntheses, the latter approach is increasingly important. Although various amino cation equivalents have been suggested,[7] their application to carboxylic acid derivatives is still limited.[8] In the course of the study of α-arylation of ketones with diazonium salts, we have found that an amino group can be efficiently introduced onto the α-carbon of esters through the reaction of ketene silyl ketals with diazonium salts.[9]


(1)

(2)

(3)

Scheme 1
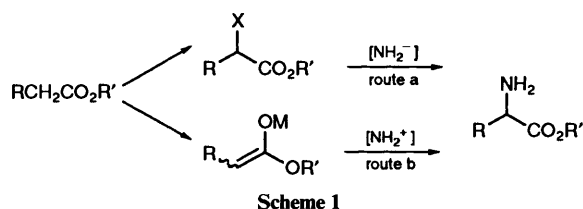
Results and Discussion

As was reported in the preceding paper, silyl enol ethers of ketones react with diazonium salts in pyridine to give α-aryl ketones with loss of dinitrogen. Based on this observation, we first expected the introduction of an aryl group onto the α-position of esters through the reaction of ketene silyl ketals (silyl enol ethers derived from esters) with diazonium salts. Under the same conditions as those for the α-arylation of ketones, however, the reaction of a ketene silyl ketal in pyridine afforded an α-hydrazono ester (E/Z mixture) as an over-whelmingly major product with a trace of a phenylated ester [eqn. (1)]. The preferential formation of hydrazone 1 rather than compound 2 seems to be due to the higher nucleophilicity of ketene silyl ketals compared with that of silyl enol ethers. Comparison of the reactivity in toluene, which is inert to the diazonium salt, also clearly revealed the higher nucleophilicity of the ketene silyl ketal as exemplified in eqns. (2) and (3). Accordingly, even in pyridine, ketene silyl ketals are envisaged
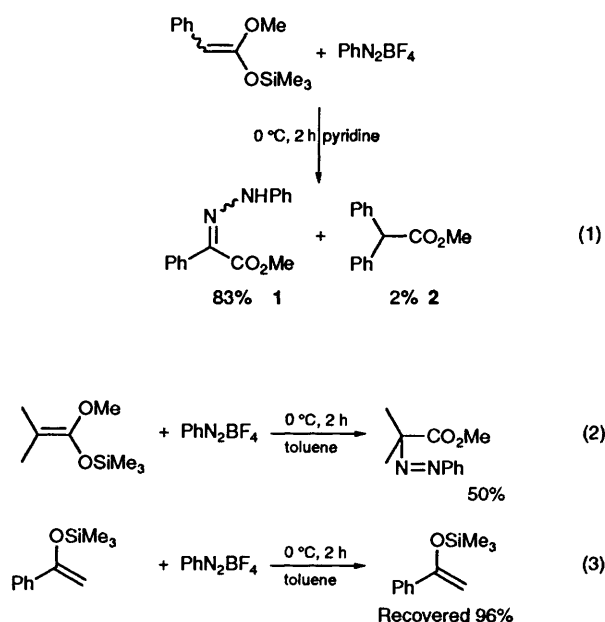
to attack preferentially diazonium salts as such (route i, Scheme 2) before the homolytic decomposition of diazonium salts (route ii).[10] In contrast, the reaction of silyl enol ethers of ketones, due to insufficient nucleophilicity, proceeds via route ii resulting in phenylated products.†

The use of pyridine as solvent is a prerequisite in order for the α-arylation of ketones to proceed effectively through the radical mechanism.† On the other hand, since the present reaction proceeds through a non-radical mechanism without releasing dinitrogen, there is no necessity to use pyridine solvent. Indeed, both mono- and di-substituted ketene silyl ketals react with diazonium salts in various solvents to give α-hydrazono and α-

Scheme 2
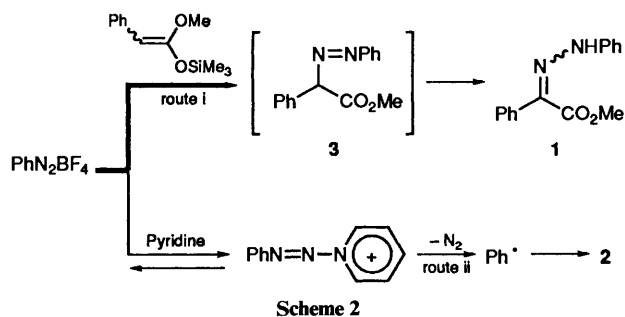
† See the preceding paper for details.

azo esters in high yields (Table 1), although pyridine also seems to be one of the best solvents for this reaction.

The present procedure is applicable to various mono- and di-substituted ketene silyl ketals with aryl, heteroaryl, aralkyl and alkyl groups (Table 2). Monosubstituted ketene silyl ketals yielded α-hydrazono esters in good yields (entries 1–4). The stereochemistry of the resulting hydrazono esters was assigned on the basis of NMR and IR data; the hydrogen bonding between C=O and N–H groups, which forms a six-membered ring, lowers the v_{CO}-value in the IR spectrum, and shifts NH signals in the NMR spectrum to lower fields (see the Experimental section for details).

Table 1 Solvent effect on formation of α-azo and α-hydrazono esters from a ketene silyl ketal and a diazonium salt

Solvent	Yield (%)
Azo ester synthesis[a]	
Pyridine	90
THF	88
MeCN	85
2,4,6-Trimethylpyridine	82
DMF	80
Dichloromethane	68
HMPA	51
Hydrazono ester synthesis[b]	
THF	88
Pyridine	83
MeCN	63

[a] $Me_2C=C(OMe)(OSiMe_3)$ (2.0 mmol), PhN_2BF_4 (2.6 mmol), solvent (6 cm³), 0 °C, 2 h. The yields were evaluated by GLC. [b] Ph(H)C=C(OMe)(OSiMe_3) (2.0 mmol), PhN_2BF_4 (2.6 mmol), solvent (6 cm³), 0 °C, 2 h. The yields were determined after isolation by column chromatography.

The hydrazono esters were most likely produced as secondary products *via* the isomerization of the α-azo esters which were primarily formed by the nucleophilic attack of ketene silyl ketals on the terminal nitrogen of diazonium salts (Scheme 2). Indeed, the crude reaction mixture of entry 1, Table 2 seemed to contain the α-azo ester 3 as the major component as judged from NMR and IR spectroscopy (see the Experimental section). IR spectra of the other reaction mixtures also showed the formation of α-azo esters as major components. However, the isolated products were α-hydrazono esters in all cases. The isomerization to the hydrazono esters presumably took place during purification by silica gel chromatography. This assumption is in agreement with the fact that α-azo esters were isolated in the reaction of disubstituted ketene silyl ketals; the isomerization of an azo to a hydrazono form is impossible.

The yields of α-azo esters obtained from disubstituted ketene silyl ketals were excellent, irrespective of the reactive substituents (entries 5–7). The presence of bulky substituents on the oxygen (phenoxy and dimethylphenylsiloxy groups) did not hamper the reaction (entry 6). The effect of the electronic nature of diazonium salts was also small as seen in entries 7–9; azo esters were obtained in high yields regardless of the nature of the *para*-substituent of the diazonium salt.

According to the literature,[11] the reactions of diazonium salts with lithium enolates of esters or ketene alkyl ketals gave complicated mixtures of products and the yields of azo or hydrazono esters were less than 30%. In contrast, the present reaction proceeds much more selectively under mild conditions. On the other hand, the present transformation is related to the Japp–Klingemann (J.-K.) reaction, which affords hydrazono compounds from active methylenes [eqn. (4)].[12] The reaction using ketene silyl ketals surpasses the J.-K. reaction in the following respects. (1) The J.-K. reaction requires active

Table 2 Reaction of a ketene silyl ketal with an arenediazonium salt[a]

Entry	Ketene silyl ketal	Diazonium salt	Yield (%)	E/Z quotient of hydrazono ester
1	Ph, OMe / OSiMe₃	PhN_2BF_4	83	88/12
2	PhCH₂, OMe / OSiMe₃	PhN_2BF_4	76	E only
3	S, OMe / OSiMe₃	PhN_2BF_4	72	10/90[b]
4	OMe / OSiMe₃	PhN_2BF_4	59	E only
5	Ph, OMe / Et, OSiMe₃	PhN_2BF_4	90	
6	Et, OPh / OSiMe₂Ph	PhN_2BF_4	90	
7	OMe / OSiMe₃	PhN_2BF_4	92	
8		p-ClC₆H₄N₂BF₄	72	
9		p-MeOC₆H₄N₂BF₄	84	

[a] Ketene silyl ketal (2.0 mmol), diazonium salt (2.6 mmol), pyridine (6 cm³), 0 °C, 2 h. Yields and E/Z quotients were determined after isolation. [b] Note that the preferred configuration is essentially the same as in the other cases; the formal reversal in the E/Z quotient is associated with the Cahn–Ingold–Prelog priority rule.

methylenes having two electron-withdrawing groups, whereas the present reaction can start from simple esters. (2) The J.–K. reaction cannot be applied to the synthesis of α-substituted α-amino acids, which are easily obtained by the present method through α-azo esters (vide infra).
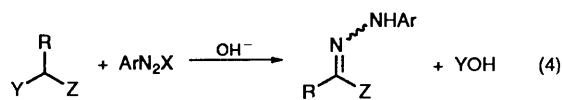

Y, Z: Electron-withdrawing group (e.g., COMe, CO₂Me, etc.)

Finally, the transformation of hydrazono and azo esters into amino esters was achieved. The simple hydrogenation of hydrazono esters to amino esters has already been reported by Khan and Kidwai using a Pd/C catalyst.[13] α-Azo and α-hydrazono esters were easily hydrogenated under mild conditions to give the corresponding α-amino esters in quantitative yields [eqns. (5) and (6)].
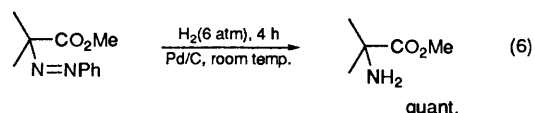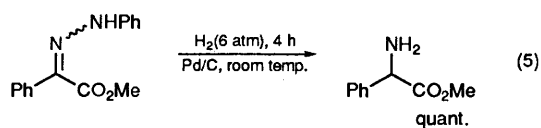
Conclusions.—We have provided a convenient and selective method for converting simple esters into α-amino esters by using easily available diazonium salts as amino cation equivalents. Diastereoselective amination of ester enolates by introducing an asymmetric centre will be central to our next investigation.[8] It is worth noting again that diazonium salts can also behave as aryl-cation equivalents in the reaction with silyl enol ethers of ketones. These results clearly exhibit the high utility of the dichotomous character of diazonium salts (Scheme 3).
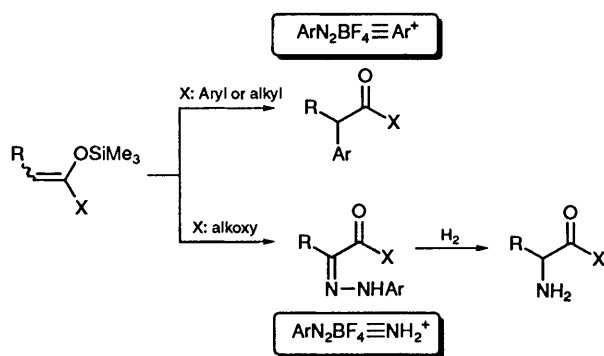
Scheme 3

Experimental

General.—IR spectra were recorded on a JASCO A-302 spectrometer. ^{1}H NMR spectra were measured in CDCl₃ on a Hitachi R-40 (90 MHz) spectrometer. ^{1}H NMR signals were referred to tetramethylsilane as internal standard, and J values are given in Hz. Mass spectra were obtained on a Shimadzu QP-1000 spectrometer. M.p.s (hot-stage) and b.p.s were not corrected. Elemental analyses were carried out by the Institute of Physical and Chemical Research, Wako, Japan. GLC analyses were performed with 3% OV-101 on Chromosorb WHP as column packing.

Reagents.—Diazonium salts were prepared and treated as described in the preceding paper. The following ketene silyl ketals were prepared according to the literature methods[14] and the structures were confirmed by NMR and IR spectroscopy: 1-methoxy-1-(trimethylsiloxy)prop-1-ene, 1-methoxy-2-phenyl-1-(trimethylsiloxy)ethene and 1-methoxy-2-methyl-1-(trimethylsiloxy)prop-1-ene. The other ketene silyl ketals were synthesized through enolization of the corresponding esters with LDA, followed by silylation with chlorotrimethylsilane. Their physical properties are shown below.

1-Methoxy-2-(2-thienyl)-1-(trimethylsiloxy)ethene (a mixture of E and Z forms, major:minor = 3:2). B.p. 150 °C (20 mmHg, Kugelrohr); ν_{max}(CCl₄)/cm⁻¹ 1652 (C=C); major isomer δ_H 0.30 (9 H, s, SiMe₃), 3.68 (3 H, s, OMe), 5.05 (1 H, s, CH) and 6.7–7.1 (3 H, m, C₄H₃S); minor isomer δ_H 3.61 (3 H, s, OMe) and 5.00 (1 H, s, CH) (Found: C, 52.3; H, 6.9. C₁₀H₁₆O₂SSi requires C, 52.6; H, 7.1%).

1-Methoxy-2-phenyl-1-(trimethylsiloxy)but-1-ene (a mixture of E and Z forms, major:minor = 3:2). B.p. 56–57 °C (0.12 mmHg); ν_{max}(CCl₄)/cm⁻¹ 1665 (C=C); major isomer δ_H 0.00 (9 H, s, SiMe₃), 0.98 (3 H, t, J 8, CH₂Me), 2.44 (2 H, q, J 8, CH₂Me), 3.65 (3 H, s, OMe) and 7.1–7.5 (5 H, m, Ph); minor isomer δ_H 0.31 (9 H, s, SiMe₃), 0.94 (3 H, t, J 8, CH₂Me), 2.39 (2 H, q, J 8, CH₂Me) and 3.46 (3 H, s, OMe) (Found: C, 66.8; H, 8.9. C₁₄H₂₂O₂Si requires C, 67.15; H, 8.9%).

1-Methoxy-3-phenyl-1-(trimethylsiloxy)prop-1-ene (a mixture of E and Z forms, major:minor = 8:1). B.p. 135 °C (5 mmHg); ν_{max}(CCl₄)/cm⁻¹ 1678 (C=C); major isomer δ_H 0.23 (9 H, s, SiMe₃), 3.33 (2 H, d, J 7, PhCH₂), 3.53 (3 H, s, OMe), 3.90 (1 H, t, J 7, CH) and 7.23 (5 H, s, Ph); minor isomer δ_H 3.50 (3 H, s, OMe) (Found: C, 65.7; H, 8.6. C₁₃H₂₀O₂Si requires C, 66.05; H, 8.5%).

2-Methyl-1-phenoxy-1-(dimethylphenylsiloxy)but-1-ene (a mixture of E and Z forms, major:minor = 3:2). B.p. 130 °C (0.6 mmHg); ν_{max}(CCl₄)/cm⁻¹ 1705 (C=C); major isomer δ_H 0.36 (6 H, s, SiMe₂), 0.98 (3 H, t, J 8, CH₂Me), 1.49 (3 H, s, Me), 2.10 (2 H, q, J 8, CH₂Me) and 6.8–7.6 (10 H, m, Ph); minor isomer δ_H 0.88 (3 H, t, J 8, CH₂Me), 1.63 (3 H, s, Me) and 1.95 (2 H, q, J 8, CH₂Me) (Found: C, 72.95; H, 7.7. C₁₉H₂₄O₂Si requires C, 73.0; H, 7.7%).

Typical Reaction.—Benzenediazonium tetrafluoroborate (2.60 mmol) was added to a pyridine solution (6 cm³) of a ketene silyl ketal (2.00 mmol) at 0 °C under nitrogen. After 2 h, diethyl ether (30 cm³) was added to the reaction mixture. The solution was washed successively with 1.5 mol dm⁻³ aq. hydrochloric acid (60 cm³), water (20 cm³) and saturated aq. NaCl (20 cm³), and dried over magnesium sulfate. The ethereal solution was evaporated and the residue was purified by silica gel column chromatography. When the isolation step was not required, the reaction mixture was analysed by GLC after addition of octadecane (200 mg, GLC internal standard).

Properties of the isolated α-hydrazono or α-azo esters are listed below.

Methyl 2-[(E)-phenylhydrazono]propionate. M.p. 93.5 °C (from hexane) (lit.,[15] 94–95 °C); ν_{max}(CHCl₃)/cm⁻¹ 1704 (CO₂Me) and 1579 (C=N); δ_H 2.03 (3 H, s, CMe), 3.80 (3 H, s, OMe), 6.8–7.2 (5 H, m, Ph) and 8.06 (1 H, br s, NH).

Methyl 2-phenyl-2-[(Z)-phenylhydrazono]acetate. M.p. 86–87 °C (from hexane) (lit.,[16] 86–88 °C); ν_{max}(melt)/cm⁻¹ 1680 (CO₂Me) and 1530 (C=N); δ_H 3.85 (3 H, s, OMe), 6.9–7.9 (5 H, m, Ph) and 12.42 (1 H, br s, NH).

Methyl 2-phenyl-2-[(E)-phenylhydrazono]acetate. M.p. 118–119 °C (from hexane); ν_{max}(KBr)/cm⁻¹ 1714 (CO₂Me) and 1550 (C=N); δ_H 3.85 (3 H, s, OMe), 6.8–7.8 (10 H, m, Ph) and 8.15 (1 H, br s, NH) (Found: C, 70.7; H, 5.5; N, 10.9. C₁₅H₁₄N₂O₂ requires C, 70.85; H, 5.55; N, 11.0%).

Methyl 3-phenyl-2-[(E)-phenylhydrazono]propionate. M.p.

Table 3

Method	(E)-form	(Z)-form
TLC	smaller R_f-value	larger R_f-value
v_{max}/cm^{-1} (CO₂R)	higher ($\geqslant 1700$)	lower ($\leqslant 1700$)
(C=N)	higher ($\geqslant 1550$)	lower ($\leqslant 1550$)
δ_H (NH)	smaller ($\leqslant 9$)	larger ($\geqslant 12$)

87–89 °C (from hexane); $v_{max}(CHCl_3)/cm^{-1}$ 1706 (CO₂Me) and 1574 (C=N); δ_H 3.88 (3 H, s, OMe), 4.06 (2 H, s, PhCH_2), 6.8–7.4 (10 H, m, Ph) and 8.09 (1 H, br s, NH) (Found: C, 71.6; H, 6.0; N, 10.3. $C_{16}H_{16}N_2O_2$ requires C, 71.6; H, 6.0; N, 10.4%).

Methyl 2-[(E)-phenylhydrazono]-2-(2-thienyl)acetate. M.p. 77–78 °C (from hexane); $v_{max}(CHCl_3)/cm^{-1}$ 1684 (CO₂Me) and 1525 (C=N); δ_H 3.95 (3 H, s, OMe), 6.8–7.6 (8 H, m, C_4H_3S and Ph) and 12.5 (1 H, br s, NH) (Found: C, 59.9; H, 4.6; N, 10.6. $C_{13}H_{12}N_2O_2S$ requires C, 60.0; H, 4.65; N, 10.8%).

Methyl 2-[(Z)-phenylhydrazono]-2-(2-thienyl)acetate. M.p. 85–86 °C (from hexane); $v_{max}(CHCl_3)/cm^{-1}$ 1710 (CO₂Me) and 1555 (C=N); δ_H 3.86 (3 H, s, OMe), 6.8–7.7 (8 H, m, C_4H_3S and Ph) and 8.73 (1 H, br s, NH) (Found: C, 59.9; H, 4.6; N, 10.6%).

Methyl 2-methyl-2-(phenylazo)propionate. $v_{max}(neat)/cm^{-1}$ 1740 (CO₂Me); δ_H 1.59 (6 H, s, Me), 3.71 (3 H, s, OMe) and 7.3–7.8 (5 H, m, Ph) (Found: C, 63.9; H, 6.8; N, 13.4. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.8; N, 13.6%).

Methyl 2-phenyl-2-(phenylazo)butyrate. $v_{max}(neat)/cm^{-1}$ 1740 (CO₂Me); δ_H 0.83 (3 H, t, J 7, CH₂Me), 2.43 (2 H, q, J 7, CH_2Me), 3.65 (3 H, s, OMe) and 7.2–8.0 (10 H, m, Ph) (Found: C, 72.1; H, 6.4; N, 10.0. $C_{17}H_{18}N_2O_2$ requires C, 72.3; H, 6.4; N, 9.9%).

Phenyl 2-methyl-2-(phenylazo)butyrate. $v_{max}(neat)/cm^{-1}$ 1760 (CO₂Ph); δ_H 1.13 (3 H, t, J 8, CH₂Me), 1.65 (3 H, s, CMe), 2.30 (2 H, q, J 8, CH_2Me) and 7.0–8.0 (10 H, m, Ph) (Found: C, 72.2; H, 6.3; N, 9.8%).

Methyl 2-(4-chlorophenylazo)-2-methylpropionate. $v_{max}(neat)/cm^{-1}$ 1744 (CO₂Me); δ_H 1.57 (6 H, s, Me), 3.74 (3 H, s, OMe), 7.43 (2 H, d, J 9, ArH) and 7.70 (2 H, d, J 9, ArH) (Found: C, 54.8; H, 5.4; N, 11.9. $C_{11}H_{13}ClN_2O_2$ requires C, 54.9; H, 5.4; N, 11.6%).

Methyl 2-methyl-2-(4-methoxyphenylazo)propionate. $v_{max}(neat)/cm^{-1}$ 1742 (CO₂Me); δ_H 1.56 (6 H, s, Me), 3.73 (3 H, s, OMe), 3.82 (3 H, s, OMe), 6.93 (2 H, d, J 9, ArH) and 7.72 (2 H, d, J 9, ArH) (Found: C, 60.8; H, 6.7; N, 11.6. $C_{12}H_{16}N_2O_3$ requires C, 61.0; H, 6.8; N, 11.9%).

Assignment of E and Z forms of α-Hydrazono Esters.—Methyl 2-(phenylhydrazono)propionate was synthesized from methyl pyruvate and phenylhydrazine according to the literature method.[15] The obtained mixture was purified by TLC [hexane–diethyl ether (2:1)] to separate E and Z forms. The analytical data of the isolated hydrazono esters are shown below.

Methyl 2-[(E)-phenylhydrazono]propionate. R_f-Value [hexane–diethyl ether (2:1)] 0.24; m.p. 92.5 °C (from hexane) (lit.,[15] 94–95 °C); $v_{max}(KBr)/cm^{-1}$ 3320 (NH), 1708 (CO₂Me) and 1565 (C=N); δ_H 2.08 (3 H, s, CMe), 3.83 (3 H, s, OMe), 6.8–7.5 (5 H, m, Ph) and 7.85 (1 H, br s, NH).

Methyl 2-[(Z)-phenylhydrazono]propionate. R_f [hexane–di-

ethyl ether (2:1)] 0.75; $v_{max}(neat)/cm^{-1}$ 3260 (NH), 1682 (CO₂Me) and 1553 (C=N); δ_H 2.12 (3 H, s, CMe), 3.74 (3 H, s, OMe), 6.7–7.7 (5 H, m, Ph) and 12.04 (1 H, br s, NH).

Based on these data, the stereroisomerism of α-hydrazono esters was assigned by the following criteria shown in Table 3.

Isomerization of α-Azo Ester to α-Hydrazono Ester.—The crude product mixture arising from 1-methoxy-2-phenyl-1-(trimethylsiloxy)ethene and PhN₂BF₄ showed a strong IR absorption for an ester group at 1747 cm⁻¹. This wavenumber is clearly higher than that of the α-hydrazono esters and very close to the values observed for α-azo esters. The NMR data for the crude mixture were also consistent with the structure of methyl 2-(phenylazo)acetate: $\delta_H(C_6D_6)$ 7.0–8.0 (10 H, m, Ph), 5.70 (1 H, s, CHN₂Ph) and 3.29 (3 H, s, CO₂Me). TLC analysis [hexane diethyl ether (5:1)] also showed the major spot with a different R_f-value (0.37) from the (E)- and (Z)-hydrazono esters (0.14 and 0.49, respectively). Putting these facts together, we conclude that the primary product in this reaction was the α-azo ester.

The major primary products resulting from 1-methoxy-3-phenyl-1-(trimethylsiloxy)prop-1-ene and 1-methoxy-2-methyl-1-(trimethylsiloxy)prop-1-ene were also α-azo esters as judged by IR spectroscopy of the crude products. In all the above cases, however, the products isolated by chromatography (silica gel) were α-hydrazono esters.

Hydrogenation of α-Hydrazono and α-Azo Esters.—Into a Schlenk-type stainless steel autoclave (27 cm³) were placed 5% Pd/C (0.05 mg-atom), methyl 2-phenyl-2-[(Z)-phenylhydrazono]acetate (1.0 mmol) and methanol (5 cm³). The reaction mixture was stirred under hydrogen (6 atm) at room temperature for 4 h. The catalyst was filtered off and was washed with methanol. The filtrate was concentrated under reduced pressure and the resulting oil was purified by TLC [hexane–diethyl ether (1:1)] to give methyl 2-amino-2-phenylacetate as needles (85%), m.p. 32–32.5 °C (from pentane) (lit.,[17] 32 °C). The corresponding (E)-form was treated similarly to give methyl 2-amino-2-phenylacetate (95%).

Methyl 2-methyl-2-(phenylazo)propionate was hydrogenated as above. GLC analysis revealed quantitative formation of methyl 2-amino-2-phenylpropionate; the structure was identified by comparison with an authentic sample.[18]

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