73. Diazoaldehyde Chemistry

Part 4[1])

Vilsmeier-Haack Formylation of Diazo Compounds: A Re-investigation

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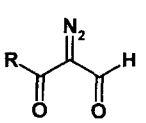
Diazomethyl ketones (2-diazoethanones) were reacted with the *Vilsmeier* reagent ((chloromethylidene)dimethylammonium chloride) to yield α-diazo-β-oxoaldehydes and chloromethyl ketones. 2',4'-Dimethoxy-α-diazoacetophenone gave 2-chloro-1-(2,4-dimethoxyphenyl)-3-(dimethylamino)prop-2-en-1-one (**5**) in addition to the expected products. Phenyldiazomethanes gave the corresponding benzyl chlorides but not the (phenyl)diazoacetaldehydes even at temperatures as low as −60°. The diazo-transfer reactions of phenylacetaldehydes and 2-azido-1-ethylpyridin-1-ium tetrafluoroborate also did not yield the expected(phenyl)diazoacetaldehydes.

Introduction. – α-Diazo-β-oxoaldehydes (**1**) are valuable synthetic tools with their interesting chemical behavior. In the first part of this series, we reported a fairly general synthetic method for these compounds using a novel diazo-transfer reaction (*Scheme 1*) [2]. On the other hand, the first report on their synthesis came from *Stojanovic* and *Arnold* almost thirty years ago (*Scheme 2*) [3], seven years after *Bosshard* and *Zollinger* had shown in this journal that the *Vilsmeier* reactions are due to the intermediate formation of (chloromethylidene)dimethylammonium chloride from dimethylformamide and thionyl chloride (or sulfuryl chloride) [4]. Although the method was low yielding, it was applied to the syntheses of etyhl α-diazo-α-formylacetate and 2-diazo-3-oxo-3-phenylpropanol which were the only successful examples. Since it had no alternatives, it has been used so far for the synthesis of those compounds. In his papers, *Arnold* reported that similar formylations of diazoacetone [3], diazoacetaldehyde [5], and phenyldiazomethane [3] had not given any identifiable products. Our method was also not successful in certain cases: β-oxoaldehydes (**2**) possessing electron-releasing R groups such as 2,4-dimethoxyphenyl, *t*-Bu, and furyl have a high tendency to undergo deformylation during the diazo transfer reaction, thus yielding diazomethyl ketones (**3**) to a higher extent than



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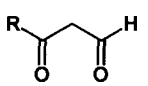

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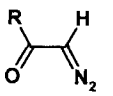

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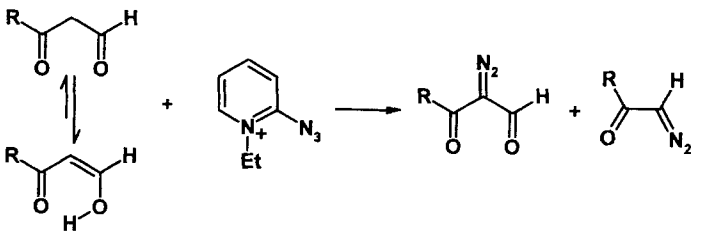
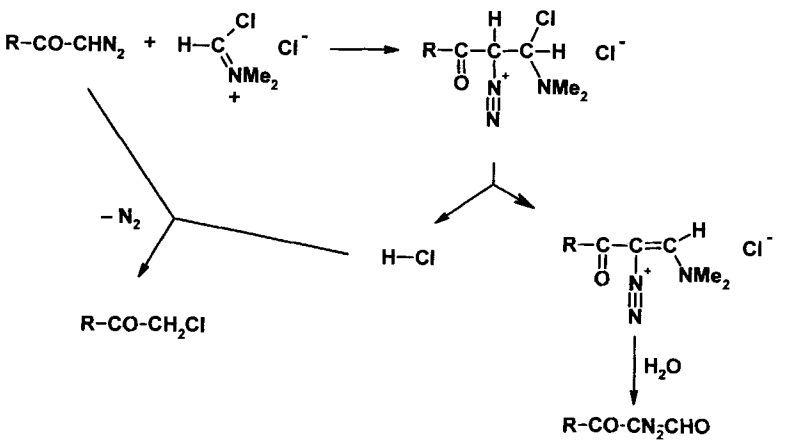
α-diazo-β-oxoaldehydes, a fact which is not avoidable because of the reaction mechanism [2]. Therefore, we thought that it would be interesting to investigate the scope and limitations of *Arnold*'s formylation reaction and the products from the formylations of diazoacetone and phenyldiazomethane.

Scheme 1

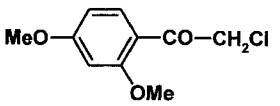


Scheme 2



Results and Discussion. – In this work, we performed the formylations of several diazomethyl ketones (**3**) with aliphatic, aromatic, and heterocyclic acyl groups (R = Me, i-Pr, i-Bu, *t*-Bu, 4-Me–C_6H_4, 4-MeO–C_6H_4, 2,4-$(MeO)_2$–C_6H_3, 1-$C_{10}H_7$, 2-$C_{10}H_7$, 2-furyl, 2,5-Me_2-3-furyl, 3,5-Me_2-2-furyl, thien-2-yl, 1-Me-pyrrol-2-yl, 1-Me-pyrrol-3-yl).

All of the diazomethyl ketones gave the diazooxoaldehydes. These included diazoacetone, which yielded no identifiable products in the hands of *Arnold*. Diazoacetone gave acetyldiazoacetaldehyde in 15% yield and chloroacetone in 50% yield. The only other attempt to detect the chloromethyl ketone by-products resulted in the isolation of 2,4-dimethoxyphenacyl chloride (**4**) from the reaction of 2,4-dimethoxydiazoacetophenone. The aqueous phase of this reaction yielded the chloroenamino ketone **5**. This compound obviously arises from the competitive N/Cl substitution *vs.* iminium-salt hydrolysis.



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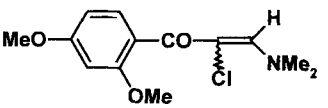

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This reaction provides an easy method to synthesize the diazooxoaldehydes which are otherwise not accessible *via* the diazo-transfer reaction [2]. The yields and spectral characteristics of the compounds obtained are shown in the *Table*. All spectral details are given in the *Exper. Part*.

Table. *Yields and Spectral Characteristics of the Diazooxoaldehydes R–CO–CN$_2$–CHO* **1**

R	Yield [%]	IR ν(CN$_2$) [cm^{-1}]	^{1}H-NMR δ(CHO) [ppm]	^{13}C-NMR δ(CN$_2$) [ppm]
Me[a])	14	2135, 2162 (sh)	9.74	49.48
Me$_2$CH[b])	27	2138, 2168	9.79	37.47
Me$_3$C[b])	44	2116, 2157	9.99	44.49
Me$_2$CH–CH$_2$[b])	21	2133, 2158 (sh)	9.78	48.25
4-Me–C$_6$H$_4$[b])	66	2133, 2164	9.78	85.65
4-MeO–C$_6$H$_4$[b])	49	2137, 2164	9.81	85.80
2,4-(MeO)$_2$–C$_6$H$_3$[b])	20	2139	9.67	Not obs.
Naphthalene-1-yl[b])	41[c])	2140, 2159	9.53	81.90
Naphthalene-2-yl[b])	35	2129, 2164	9.83	86.66
Furan-2-yl	30	2100 (sh), 2137	10.10	82.41
3,5-Me$_2$-Furan-2-yl[b])	19	2110, 2130, 2155	10.12	81.60
2,5-Me$_2$-Furan-3-yl	17	2110 (sh), 2139	9.86	81.27
Thiophen-2-yl	21	2125, 2157	9.98	84.41
N-Me-Pyrrol-2-yl	12	2137	9.94	83.90
N-Me-Pyrrol-3-yl	15	2139	9.99	83.75

[a]) *Cf.* [2] [9].
[b]) *Cf.* [2].
[c]) Impure oil.

The diazo stretching bands appeared between 2170 and 2120 cm^{-1} mostly as pairs, while those of the diazomethyl ketones are usually observed between 2100 and 2110 cm^{-1} as singlets. The *N*-methylpyrrol-1-yl and -2-yl compounds are in sharp contrast to this general observation. The higher frequency (in comparison with those of the diazomethyl ketones) C=O stretching bands of the diazooxoaldehydes are usually more intense than their diazo bands.

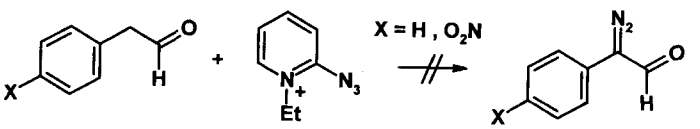
The ^{1}H-NMR chemical shifts of the aldehydic protons appeared between 9.75 and 9.85 ppm. In the cases of the heterocyclic derivatives and pivaloyldiazoacetaldehyde, the signals were detected mostly above 9.95 ppm. In the ^{13}C-NMR spectra, the signals due to the CN$_2$ C-atoms were fairly weak, being around the noise level in some cases. The aliphatic compounds gave these signals around 40–50 ppm, while the aromatics and the heterocycles displayed signals between 81 and 86 ppm relative to TMS.

It was only when the probe temperature was below 100° that the CI-MS of the aliphatic diazoaldehydes showed the monoprotonated molecular-ion signal clearly. At high temperatures (*i.e.*, above 200°), the spectra became highly crowded by the occurrence of high-molecular signals. The aromatic and heterocyclic derivatives delivered simpler spectra. On the other hand, the EI mass spectra were usually very complex because of the presence of high-molecular-mass signals, and the molecular-ion signals were hardly detectable in most cases.

Both phenyldiazomethane and 4-nitrophenyldiazomethane gave, upon formylation, the corresponding benzyl chlorides. The same result was also encountered for (4-nitrophenyl)diazomethane upon formylation at −20° and at around −55 to −60° with inverse addition of the reactants to each other. Such a result is expected for phenyldiazomethane, but it is interesting that the 4-NO_2 derivative (the diazo-bearing C-atom of which is attached to an electron-withdrawing group) did not yield any diazoaldehyde. Along with benzyl chloride, a compound, the structure of which was left unidentified, was also isolated from the reaction of phenyldiazomethane.

Attempts on transdiazotizing the phenylacetaldehydes by the 2-azido-1-ethylpyridin-1-ium salt [2] to yield the phenyldiazoacetaldehydes were unsuccessful, and the starting materials were recovered from the reactions (*Scheme 3*). The syntheses of the phenyldiazoacetaldehydes are under study.

Scheme 3



Experimental Part

General. Silica gel *60* was used for the TLC separations with hexane AcOEt 5:1 as the eluant unless otherwise stated. IR Spectra [cm^{-1}]: on a *Perkin-Elmer Mattson 1000 FT-IR* spectrometer or on a *JASCO FT-IR 5300* spectrometer. NMR Spectra (δ, $CDCl_3$, ppm): on a 200-MHz *Bruker* instrument, TMS as an internal standard; the coupling constants J in Hz. ^{13}C-NMR Spectra: at 50 MHz.

Synthesis of Diazomethyl Ketones: β-Oxoaldehyde Na salts were prepared using standard *Claisen* condensation techniques. Diazomethyl ketones **3** were prepared using the *Regitz-Yates* deformylating diazo-transfer reaction [6].

2-(Diazoacetyl)-3,5-dimethylfuran: 56% yield. M.p. 68–69° (light petroleum/CCl_4 4:1). IR: 2100, 1605. ^{1}H-NMR: 2.28 (*s*, Me); 2.35 (*s*, Me); 5.86 (CHN_2); 6.02 (*s*, H–C(4)). ^{13}C-NMR: 11.30 (Me); 13.46 (Me); 53.20 (CN_2); 112.84 (C(4)); 130.33; 145.28; 154.42; 176.31 (CO).

3-(Diazoacetyl)-2,5-dimethylfuran: 55% yield. M.p. 98–100° (hexane/CCl_4). IR: 2101, 1619. ^{1}H-NMR: 2.24 (*s*, Me); 2.56 (*s*, Me); 5.44 (*s*, CHN_2); 5.98 (*s*, H–C(4)). ^{13}C-NMR: 13.15 (Me); 13.90 (Me); 54.65 (CN_2); 104.50; 120.23; 150.32; 155.41; 182.40 (CO).

2-(Diazoacetyl)-1-methylpyrrole: 65% yield. M.p. 91–95° (hexane/CCl_4). IR: 2102, 2072, 1594. ^{1}H-NMR: 3.95 (*s*, Me); 5.70 (*s*, CHN_2); 6.08 (distorted *t*, J = 2.91, 2.70, H–C(4)), 6.63 (*d*, J = 3.56, H–C(3)), 6.79 (*s*, H–C(5)). ^{13}C-NMR: 37.22 (Me); 53.57 (CN_2); 108.04; 115.41; 128.94 (C(2)); 130.44; 177.45 (CO).

3-(Diazoacetyl)-1-methylpyrrole. The compound was impure (*ca.* 80% purity) with 57% yield. M.p. 60°. IR: 2118, 2101, 1632, 1596. ^{1}H-NMR: 5.56 (*s*, CHN_2); 3.68 (*s*, Me). ^{13}C-NMR: 36.63 (Me); 52.95 (CN_2).

Synthesis of the Phenyldiazomethanes. Phenyldiazomethane was pepared according to *Yates* and *Shapiro* [7] and was employed as soln. its diazo content being determined just before use. (4-Nitrophenyl)diazomethane was prepared according to *Davies* and *Schwartz* [8] and was used in pure crystalline form.

Formylation Reaction: General Procedure. In a perfectly dried three-necked flask is placed a CH_2Cl_2 soln. of DMF (5.5 g, 75 mmol/40 ml). While stirring in a freezing mixture, 9.4 g of oxalyl chloride (0.74 mmol) was added dropwise. After the vigorous evolution of CO and CO_2 has ceased, the mixture was heated to 40° for 10 min. The mixture was then cooled to −10°, and a very concentrated soln. of the diazomethyl ketone (100 mmol) in CH_2Cl_2 was added dropwise, maintaining the temp. not higher than 10° (the *Vilsmeier* reagent is used in 50% excess). After the brisk evolution of N_2 has subsided, the mixture was stirred at r.t. for 1 h. The soln. was concentrated, and 250 ml of dry Et_2O or THF were added. In case of crystalline diazomethyl ketones, THF gave much better results. The crystals formed were filtered immediately, washed successively with dry Et_2O or THF and then dissolved in 10% aq. AcOH. (Any crystallization failure indicated the presence of unreacted diazomethyl ketone and it was harder to purify the diazooxaldehyde in such cases.) After stirring for ½ h, the mixture was extracted with CH_2Cl_2, the extract washed well with H_2O, dried ($MgSO_4$), and evaporated. In some cases, the resulting substance was almost pure **1**. Further purification of the compounds was effected by distillation *in vacuo*, or by careful recrystallization from CCl_4/hexane mixtures.

2-Diazo-3-oxobutanal: 14% yield. B.p. 42°/0.3 Torr, M.p. −9 to 6°. Spectrally identical to an authentic sample [2] [9]: IR: 2162 (sh), 2135, 1674 (sh), 1643. ^{1}H-NMR: 9.74 (*s*, CHO); 2.41 (*s*, Me). ^{13}C-NMR: 29.26 (Me); 49.48 (CN_2); 178.1 (CHO); 187.0 (CO). CI-MS (Probe temp. < 150°): 113 (25, $[M+1]^+$), 85.6 (25), 58.3 (100). CI-MS (Probe temp. > 200°): 371.4 (17), 267 (18), 195 (16), 153 (26), 141 (18), 129 (23), 113 (100, $[M+1]^+$), 85.6 (90), 58 (58).

2-Diazo-4-methyl-3-oxopentanal: 27% yield. B.p. 54°/0.3 Torr. IR: 2168, 2138, 1666, 1630. ^{1}H-NMR: 9.79 (*s*, CHO); 2.99 (*m*, Me_2CH); 1.22 (*d*, *J* = 6.68, 2 Me). ^{13}C-NMR: 18.44 (Me); 29.71 (Me_2C); 37.47 (CN_2); 180.0 (br., 2 CO). CI-MS (Probe temp. > 200°): 321 (39), 215 (36), 201 (20), 189 (87), 161 (100), 145 (28), 133 (73), 119 (92), 103 (24), 91.5 (35); Peaks with intensities between 10 and 20%: 295, 279, 265, 251, 235; molecular-ion signal (140, or 141 ($[M+1]^+$)) was not observed. EI-MS: 165 (28), 141 (7, $[M+1]^+$), 140 (7, M^+), 113 (24), 97 (25), 85 (40), 83 (28), 71 (100), 57.2 (67); Peaks with intensities between 10 and 20%: 224, 208, 198, 196, 181, 157, 155, 153, 149, 137.

2-Diazo-4,4-dimethyl-3-oxopentanal: 44% yield. Purified by prep. TLC. R_f 0.27 (hexane/Et_2O, 5:1). IR: 2157, 2116, 1672, 1652. ^{1}H-NMR: 9.99 (*s*, CHO); 1.30 (*s*, 3 Me). ^{13}C-NMR: 26.52 (3 Me); 41.73 (Me_3C); 44.49 (CN_2); 182.84 (CHO); 195.24 (CO). CI-MS (Probe Temp. < 100°): 155 (5, $[M+1]^+$), 127 (21), 72 (33), 58.3 (100). CI-MS (Probe temp. > 200°): 155 (63, $[M+1]^+$), 127 (100), 72 (64), 57.3 (75). Peaks with intensities ≤ 20%: 321, 263, 253, 237, 225, 213, 199, 111, 101, 85.6, 81.7. EI-MS: 295 (7), 281 (24), 251 (100), 236 (30), 221 (18), 207 (10), 197 (19), 167 (27), 141 (22), 115 (10), 85 (16), 74 (37), 62 (27); peaks 154 and 155 are in a crowd with other minor peaks of similar intensities (*ca.* 5–8%).

2-Diazo-5-methyl-3-oxohexanal: 21% yield. B.P. 67°/0.3 Torr. IR: 2158 (slight sh), 2133, 1675, 1645. ^{1}H-NMR: 9.78 (*s*, CHO); 2.55 (*d*, *J* = 6.91, CH_2); 2.24 (*m*, CH); 1.01 (*d*, *J* = 6.59, 2 Me). ^{13}C-NMR: 22.50 (2 Me); 25.42 (CH_2); 29.69 (Me_2C); 48.25 (CN_2, intense as the CH_2 signal); 179.90 (br., 2 CO). CI-MS (Probe temp. < 100°): 156 (32, $[M+2]^+$), 155 (96, $[M+1]^+$), 127 (100), 109 (31), 81.7 (84), 57.3 (84). CI-MS (Probe temp. > 200°): 321 (32), 253 (66), 237 (32), 225 (47), 155 (86, $[M+1]^+$), 127 (100), 85.6 (83), 57.3 (74); peaks with intensities between 7 and 20%: 295, 283, 271, 213, 206, 197, 185, 172. EI-MS: 155 (24, $[M+1]^+$), 127 (46), 112 (75), 111 (76), 97 (47), 85 (70), 84 (100), 75 (22), 69 (55), 57.2 (95).

2-Diazo-3-(4′-methylphenyl)-3-oxopropanal: 66% yield. Recrystallized from a mixture of CCl_4 and a little hexane. R_f 0.40. M.p. 68–69°. IR: 2164, 2133, 1662, 1627. ^{1}H-NMR: 2.44 (*s*, Me); 7.32 (*d*, *J* = 8.0, H–C(3′), H–C(5′)); 7.58 (*d*, *J* = 8.0, H–C(2′), H–C(6′)); 9.78 (*s*, CHO). ^{13}C-NMR: 21.54 (Me); 85.65 (CN_2); 127.97; 129.58; 133.58; 143.95; 181.69 (CHO); 184.58 (CO).

2-Diazo-3-(4′-methoxyphenyl)-3-oxopropanal: 49% yield. Recrystallized from CCl_4. M.p. 74–75°. IR: 2162, 2137, 1655, 1600. ^{1}H-NMR: 3.89 (*s*, MeO); 7.00 (*d*, *J* = 8.79, H–C(3′), H–C(5′)); 7.68 (*d*, *J* = 8.79, H–C(2′), H–C(5′)) (these two *d*'s represent an *AA′XX′* system rather than a simple pair of *d*'s); 9.81 (*s*, CHO). CI-MS: 263 (11), 205 (68, $[M+1]^+$), 179 (100), 177 (94), 161 (91), 151 (80), 135 (25), 80 (65).

2-Diazo-3-(2′,4′-dimethoxyphenyl)-3-oxopropanal: 20% yield. Recrystallized from hexane. R_f 0.78 (hexane/AcOEt, 1:1). M.p. 113–4° (dec.). IR: 2139, 1656, 1603. ^{1}H-NMR: 9.67 (*s*, CHO); 7.50 (*d*, *J* = 8.39, H–C(6′)); 6.60 (*dd*, *J* = 2.15, 8.71, H–C(5′)); 6.48 (*d*, *J* = 2.11); 3.87 (*s*, Me); 3.86 (*s*, Me). ^{13}C-NMR: 55.66; 98.52; 105.92; 132.15; 182.74; the signal for CN_2 not observed.

2-Diazo-3-(naphthalen-1′-yl)-3-oxopropanal: impure oil with 41% yield. R_f 0.37. IR: 2159, 2140, 1672, 1625. ^{1}H-NMR: 9.53 (CHO). ^{13}C-NMR: 81.90 (CN_2); 181.40 (CHO).

2-Diazo-3-(naphthalen-2′-yl)-3-oxopropanal: 35% yield. Recrystallized from hexane. R_f 0.37. M.p. 100–101°. IR: 2164, 2129, 1654, 1612. ^{1}H-NMR: 9.83 (*s*, CHO); 7.5–8.0 (*m*, arom.). ^{13}C-NMR: 86.66 (CN_2); 123.81; 126.40; 127.40; 127.98; 128.44; 128.76; 129.19; 132.35; 133.63; 135.38; 181.59 (CHO); CO signal not observed.

CI-MS: 241 (3), 239 (4), 225(6, $[M+1]^+$), 224 (M^+, 5), 223 (20), 209 (4), 197 (9), 183 (32), 171 (100), 155 (5), 113 (9), 107 (6), 97 (11), 86 (37), 82 (29), 70 (61).

2-Diazo-3-(furan-2'-yl)-3-oxopropanal: 30% yield. Recrystallized from hexane. R_f 0.21. M.p. 81–82.5°. IR: 2137, 2100 (slight sh.), 1656, 1615. ^{1}H-NMR: 6.67 (*t*-like *dd*, J = 1.66, 1.86, H–C(4')); 7.37 (*d*, J = 3.4, H–C(3')); 7.66 (*s*, H–C(5')); 10.10 (*s*, CHO). ^{13}C-NMR: 82.41 (CN_2), 112.97; 118.07; 145.99 (C(5')); 151.06 (C(1')); 170.07 (CO); 182.15 (CHO). CI-MS: 166 (34, $[M+2]^+$), 165 (100, $[M+1]^+$), 139 (31), 137 (100).

2-Diazo-3-(3',5'-dimethylfuran-2'-yl)-3-oxopropanal: 19% yield. Recrystallized from CCl_4. R_f 0.37. M.p. 75–7°. IR: 2155, 2130, 2110, 1676, 1656, 1643. ^{1}H-NMR: 10.12 (*s*, CHO); 6.12 (*s*, H–C(4')); 2.39 (*s*, Me); 2.34 (*s*, Me). ^{13}C-NMR: 11.85 (Me); 13.95 (Me); 81.6 (CN_2); 134.88; 145.13; 155.55; 170.70 (CO); 183.23 (CHO). CI-MS: 193 (72, $[M+1]^+$), 183 (21), 165 (100), 139 (88), 123 (17), 85.7 (5).

2-Diazo-3-(2',5'-dimethylfuran-3'-yl)-3-oxopropanal: 17% yield. Recrystallized from a mixture of CCl_4 and little hexane. R_f 0.40. M.p. 58–60°. IR: 2139, 2110 (slight sh), 1653, 1634. ^{1}H-NMR: 2.29 (*s*, Me); 2.51 (*s*, Me); 6.09 (*s*, H–C(4')); 9.86 (*s*, CHO). ^{13}C-NMR: 13.23 (Me); 13.86 (Me); 81.27 (CN_2); 104.63; 119.43; 151.13; 157.34; 181.95 (CHO); signal for CO not observed.

2-Diazo-3-oxo-3-(thiophen-2'-yl)propanal: 21% yield. Recrystallized from hexane. R_f 0.22. M.p. 66–67°. IR: 2157, 2125, 1662, 1624. ^{1}H-NMR: 7.20 (*t*, J = 4.4, H–C(4')); 7.67 (*d*, J = 3.86, H–C(3')); 7.76 (*d*, J = 4.66, H–C(5')); 9.98 (*s*, CHO). ^{13}C-NMR: 84.41 (CN_2); 129.20; 131.51; 133.92; 140.76 (C(2)); 175.13 (CO); 181.37 (CHO). CI-MS: 181 (100, $[M+1]^+$), 155 (35), 153 (98), 137 (9), 127 (31), 111 (13).

2-Diazo-3-(1'-methylpyrrol-2'-yl)-3-oxopropanal: 12% yield. Recrystallized from a mixture of CCl_4 and a little hexane. R_f 0.25. M.p. 48–50°. IR: 2137, 1629. ^{1}H-NMR: 3.93 (*s*, Me); 6.21 (*dd*, J = 2.40, 2.38, H–C(4')); 6.77 (*dd*, J = 1.32, 1.58, H–C(3')); 6.91 (*d*, J = 1.61, H–C(5')); 9.94 (*s*, CHO). ^{13}C-NMR: 36.95 (Me); 83.90 (CN_2); 108.81; 118.46; 131.45; 128.0 (C(2')); 173.4 (CO); 182.58 (CHO). CI-MS: 178 (100, $[M+1]^+$), 152 (72), 134 (31), 122 (73), 108 (13).

2-Diazo-3-(1'-methylpyrrol-3'-yl)-3-oxopropanal: 15% yield. Recrystallized from a mixture of CCl_4 and a little hexane. R_f 0.07. M.p. 70–2°. IR: 2139, 1664, 1641. ^{1}H-NMR: 3.73 (*s*, Me); 6.51 (*dd*, J = 1.7, 1.1, H–C(4')); 6.65 (*t*, J = 2.45, H–C(5')); 7.27 (*d*, J = 2.2, H–C(2')); 9.99 (*s*, CHO). ^{13}C-NMR: 36.81 (Me); 83.75 (CN_2); 100.17; 123.62; 126.45; 177.25 (CO); 182.77 (CHO). CI-MS: 236 (5), 198 (10), 196 (29), 178 (30, $[M+1]^+$), 162 (17), 152 (97), 150 (100), 134 (30), 132 (31), 124 (93), 108 (40), 82.7 (6).

2-Chloro-1-(2',4'-dimethoxyphenyl)ethan-1-one (**4**): The Et_2O/CH_2Cl_2 mother soln. from the reaction of 2',4'-dimethoxydiazoacetophenone was evaporated, and the residue was purified by TLC. M.p. 107–109°. R_f 0.30. IR: 1664, 1603. ^{1}H-NMR: 3.87 (*s*, MeO); 3.92 (*s*, MeO); 4.73 (*s*, CH_2Cl); 6.46 (*d*, J = 2.13, H–C(3')); 6.58 (*dd*, J = 2.25, 8.8, H–C(5')); 7.94 (*d*, J = 8.8, H–C(6')). ^{13}C-NMR: 51.14; 55.66; 98.28; 105.96; 133.66. EI-MS: 204 (51), 202 (89), 154 (97), 138 (63), 123 (51), 110 (99), 96 (95), 82 (77), 69 (99), 56.6 (100); molecular signal not observed.

2-Chloro-1-(2',4'-dimethoxyphenyl)-3-(dimethylamino)prop-2-en-1-one (**5**). The aq. mother soln. from the reaction of 2',4'-dimethoxydiazoacetophenone after filtration was extracted with CH_2Cl_2, the org. extract dried and evaporated, and the residue purified by TLC. M.p. 149–50°. R_f 0.10. IR: 1672, 1620, 1601, 1568. ^{1}H-NMR: 3.25 (*s*, Me_2N); 3.87 (*s*, MeO); 6.66 (*d*, J = 1.85, H–C(3')); 6.72 (*dd*, J = 1.85, 7.68, H–C(5')); 6.93 (*s*, H–C(3)); 7.69 (*d*, J = 8.44, H–C(6')). ^{13}C-NMR: 42.68; 55.68; 95.87; 111.02; 124.36; 130.03. EI-MS: 221 (2), 210 (1), 209 (15), 208 (92), 193 (68), 192 (69), 178 (72), 177 (70), 166 (83), 165 (100), 164 (72), 151 (53), 139 (62), 122 (55), 107.5 (42), 98.5 (63), 95.3 (34), 82.4 (13), 74.2 (59), 69 (15), 67 (15), 61 (17), 56.5 (52); M^+ signal not observed.

Diazo-Transfer Reaction to Phenylacetaldehydes. The general procedure described in [2] was employed in performing the reactions of phenyl- and (4-nitrophenyl)acetaldehyde with *in situ* prepared 2-azido-1-ethylpyridin-1-ium tetrafluoroborate. The starting materials were recovered from the reaction mixtures even after exposure to prolonged reaction times or high temp. up to 40°.

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