1,5-Diphenyl-1,4-pentadiyn-3-ol (56.0 g, 0.241 mol) was dissolved in 240 mL of acetone and cooled to ice-bath temperature. Kiliani reagent[12] was prepared by adding sodium dichromate (45 g, 0.15 mol) to a cooled solution of sulfuric acid (60 g) in 200 mL of water. This solution was added dropwise over 30 min to the diynol. The reaction mixture was poured over 1500 g of ice. The product was extracted with methylene chloride (1 × 800 mL, 2 × 200 mL). The combined methylene chloride extracts were dried over $MgSO_4$ and filtered through a short Florisil column. Concentration and recrystallization of the residue from ligroine gave 40.0 g (72%) of **2** as a yellow solid, mp 65–65 °C (lit.[11] mp 60 °C).

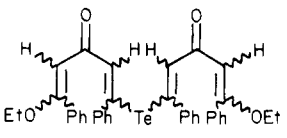
Preparation of 2,6-Diphenyl-4*H*-thiapyran-4-one (1a). Undr a nitrogen atmosphere was added 40 mL of a 1 M solution of lithium triethylborohydride in THF (0.040 mol) to sulfur (0.64 g, 0.020 mol). The reaction mixture was stirred at room temperature for 1 h, and 80 mL of a 1 M solution of sodium ethoxide in ethanol was added. The resulting solution was added dropwise over 5 min to a solution of **2** (4.60 g, 0.0200 mol) in 50 mL of THF and 50 mL of 1 M sodium ethoxide in ethanol cooled in an ice bath. After 1 h at 0 °C, the reaction mixture was stirred at room (temperature for 17 h and then concentrated in vacuo. The residue was partitioned between methylene chloride and water. The methylene chloride solution was dried over sodium sulfate and concentrated to give 5.0 g (95%) of a pale yellow solid. Recrystallization from acetonitrile gave 3.71 g (70%) of **1a** as pale yellow needles: mp 132 °C (lit.[3] mp 132–133 °C); ^1H NMR ($CDCl_3$) δ 7.0 (s, 2 H), 7.35 (m, 10 H); IR (KBr) 3050, 1600, 1580, 1560, 1450, 1348, 768, 734, 695, 686 cm^{-1}.

Preparation of 2,6-Diphenyl-4*H*-selenapyran-4-one (1b). Selenium shot (3.20 g, 0.0400 mol) was treated with 80 mL (0.080 mol) of 1 M lithium triethylborohydride for 2 h as described. The dilithium selenide in 160 mL of 1 M sodium ethoxide in ethanol was added to a solution of **2** (9.20 g, 0.0400 mol) in 100 mL of THF and 100 mL of 1 M sodium ethoxide in ethanol as described. Workup as before and recrystallization from acetonitrile gave 8.63 g (70.2%) of **1b** as a tan solid: mp 147–148 °C (lit.[3] mp 145–146 °C); ^1H NMR ($CDCl_3$) δ 7.50 (m, 10 H, 7.27 (s, 2 H); IR (KBr) 3050, 1580, 1560, 1360, 910, 875, 765, 755, 696 cm^{-1}.

Preparation of 2,6-Diphenyl-4*H*-tellurapyran-4-one (1c). A procedure similar to the ones described above was followed except that the solvents were degassed with a stream of nitrogen for 15 min before use. Tellurium shot (7.65 g, 0.0600 mol) was treated with 120 mL of 1 M lithium triethylborohydride for 4 h as described. The dilithium telluride mixture in 240 mL of 1 M sodium ethoxide in ethanol was added dropwise to a solution of **2** (13.8 g, 0.0600 mol) in 200 mL of THF and 200 mL of 1 M sodium ethoxide in ethanol as described. After 1 h at 0 °C, the reaction mixture was stirred in a 35 °C bath for 17 h. A workup as described followed by careful chromatography on silica gel (50:1 w/w, eluted with 10% ethyl acetate/methylene chloride) gave crude **1c** (R_f 0.4). Recrystallization from acetonitrile gave 10.9 g (50.5%) of a yellow crystalline solid: mp 127.5–129 °C; ^1H NMR ($CDCl_3$) δ 7.47 (m, 10 H), 7.31 (s, 2 H); IR (KBr) 1570, 1550, 1430, 1310, 902, 870, 768, 755, 698 cm^{-1}; UV (CH_2Cl_2) λ_{max} 365 nm (log ϵ 4.08); mass spectrum, m/e 362 ($C_{17}H_{12}O^{130}Te$).

Anal. Calcd for $C_{17}H_{12}OTe$: C, 56.7; H, 3.4. Found: C, 56.8; H, 3.5.

A second product (R_f 0.7) was isolated as an orange-red crystalline compound: 2.1 g (10%); mp 187–190 °C. Spectral and analytical data indicated the structure I: ^1H NMR ($CDCl_3$) δ 7.45



I

(m, 10 H), 6.80 (m, 6 H), 6.45 (s, 2 H), 6.37 (m, 4 H), 5.70 (s, 2 H), 4.03 (q, 4 H, J = 7 Hz), 1.42 (t, 6 H, J = 7 Hz); IR (KBr) 1580, 1550, 1210, 1120, 1085 cm^{-1}; mass spectrum, m/e 684 ($C_{38}H_{34}O_4{}^{130}Te$).

Anal. Calcd for $C_{38}H_{34}O_4Te$: C, 66.9; H, 5.0; Te, 18.7. Found: C, 66.7; H, 5.1; Te, 18.9.

A noncrystalline mixture of other isomers of the above structure was also isolated in a 1.1-g (6%) yield.

Preparation of 2-Benzylidene-3-oxo-5-phenyl-2,3-dihydrotellurophene (3c). To a 25-mL flask, flame dried and cooled under a stream of argon, were added **2** (0.23 g, 1.0 mmol), *tert*-butyl alcohol (0.20 g, 2.7 mmol), and 5 mL of dry THF. The resulting solution was degassed with a stream of argon for 15 min. The reaction mixture was cooled to 0 °C in an ice bath, and bis(*tert*-butyldimethylsilyl) telluride (0.41 g, 1.1 mmol) was added. A degassed 1 M solution of tetra-*n*-butylammonium fluoride in THF (2.5 mL, 2.5 mmol) was added dropwise over 5 min. The resulting mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with methylene chloride, washed with brine, filtered through a Celite pad, dried over sodium sulfate, and concentrated. The residue was purified by chromatography on silica gel (50:1 w/w, eluted with methylene chloride) to give 0.10 g (28%) of **3c** (R_f 0.7; brick-orange solid; mp 123–126 °C) and 0.07 g (19%) of **1c** (R_f 0.3). For **3c**: ^1H NMR ($CDCl_3$) δ 8.40 (s, 1 H), 7.43 (m, 10 H), 7.25 (s, 1 H); IR (KBr) 1630, 1540, 1440, 1240, 1175, 762 cm^{-1}; UV (CH_2Cl_2) λ_{max} 340 nm (log ϵ 4.28), 470 (3.58); mass spectrum, m/e 362 ($C_{17}H_{12}O^{130}Te$).

Anal. Calcd for $C_{17}H_{12}OTe$: C, 56.7; H, 3.4. Found: C, 56.8; H, 3.5.

Registry No. 1a, 1029-96-5; **1b**, 52774-25-1; **1c**, 80697-46-7; **2**, 15814-30-9; **3c**, 81028-19-5; I, 81064-44-0; ethyl bromide, 74-96-4; phenylacetylene, 100-42-5; sulfur, 7704-34-9; selenium, 7782-49-2; bis(*tert*-butyldimethylsilyl)telluride, 80594-86-1.

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Novel Rearrangement of 1,2,4-Oxadiazoles to 1,2,4-Triazolinones

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It is well-known that 1,2,4-oxadiazoles undergo ring rearrangements to various other heterocyclic compounds, such as 1,2,3-triazoles,[1-3] 1,2,5-oxadiazoles,[3-8] imidazoles,[9] 1,2,4-triazoles,[10,11] benzisoxazoles,[12] 1,2,4-thiadiazoles,[13] and indazoles.[14] We now report a novel rearrangement of 3-(arylamino)-1,2,4-oxadiazoles **1** leading to 2-aryl-1,2,4-triazolin-3-ones **2**.

In the presence of sodium methoxide in methanol, oxadiazole[15] **1a** rearranged smoothly to triazolinone **2a** (Scheme I). The structure of **2a** was inferred by the consistency of its spectral features with those reported in the literature[16,17] and was subsequently confirmed by X-ray crystallographic methods. Substitutions on the phenyl ring

(1) M. Ruccia and D. Spinelli, *Gazz. Chim. Ital.*, **89**, 1654 (1959).
(2) M. Ruccia and N. Vivona, *Ann. Chim. (Rome)*, **57**, 680 (1967).
(3) P. Gramantieri, *Gazz. Chim. Ital.*, **65**, 102 (1935).
(4) E. Durio and S. Dugone, *Gazz. Chim. Ital.*, **66**, 139 (1936).
(5) G. Ponzio, *Gazz. Chim. Ital.*, **61**, 138 (1931).
(6) G. Ponzio and L. Avogadro, *Gazz. Chim. Ital.*, **53**, 318 (1923).
(7) G. Ponzio and G. Ruggeri, *Gazz. Chim. Ital.*, **53**, 297 (1923).
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(10) M. Ruccia, N. Vivona, and G. Cusmano, *J. Heterocycl. Chem.*, **8**, 137 (1971).
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(12) K. Harsanyi, *J. Heterocycl. Chem.*, **10**, 957 (1973).
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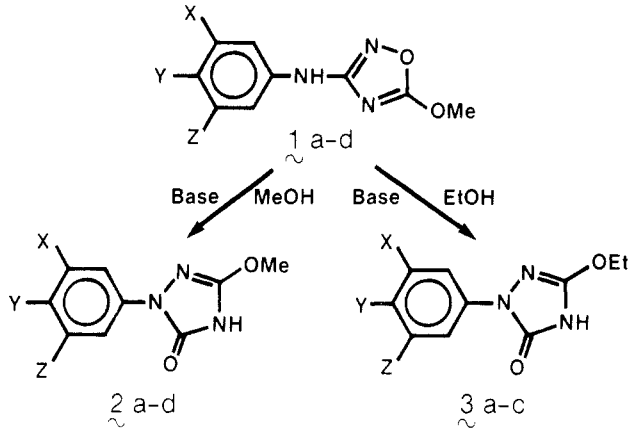
0022-3263/82/1947-1969$01.25/0

Scheme I



a) X = Y = Z = H
b) X = Cl, Y = Z = H
c) X = Z = Cl, Y = H
d) X = Z = H, Y = nBu

with chlorines or alkyl groups did not affect the rearrangement. Thus **1b**, **1c**, and **1d** rearranged very smoothly to **2b**, **2c**, and **2d**, respectively, in methanol in the presence of base. The structures of compounds **2b–2d** were elucidated on the basis of their ^{13}C NMR, ^{1}H NMR, IR, and mass spectra. Predicted ^{13}C NMR chemical shifts, calculated[18] (phenyl carbons) and assigned from models[19] (aliphatic carbons), agreed closely with experimental data (cf. Table I). In the presence of base in ethanol, oxadiazoles **1** rearrange similarly to the corresponding 5-ethoxytriazolinones **3**. Such rearrangements were not observed when oxadiazoles **1** were treated with base in nonnucleophilic solvents such as toluene and methylene chloride.

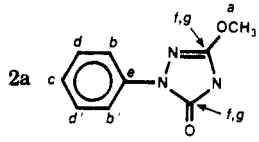
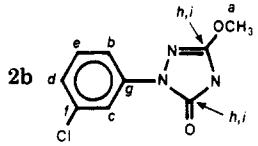
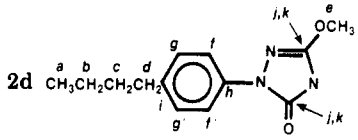
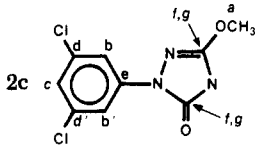
An attractive rationalization of this rearrangement is the initial formation of *N*-aryldiazirine **4**,[20] followed by diazirine ring opening by solvent (methanol or ethanol) and then ring closure to give 2-aryl-5-alkoxy-1,2,4-triazolin-3-ones **2** or **3** (Scheme II).

Thermolysis of oxadiazoles **1** gave many decomposition products; however, none of the isomeric 1,2,4-triazolin-3-ones **2** were detected. Oxadiazoles with substitution groups other than alkoxy at C5, such as 3-anilino-5-phenyl-1,2,4-oxadiazole, when subjected to alcoholic base treatment at reflux temperatures did not undergo rearrangement. The starting material was recovered quantitatively. The failure of this rearrangement is not clear so far and is left for future study.

In refluxing aqueous base, oxadiazoles **1** hydrolyzed to the corresponding 1,2,4-oxadiazol-5-ones **5** (Scheme III);[21] however, triazolinones **2** or **3** remained unchanged in aqueous base even at prolonged heating.

The structure and conformation of **2a** were elucidated by X-ray crystallographic methods. The phenyl ring system is strictly planar and shows no unusual features. The triazolinone ring system is planar within 0.008 Å and does not exhibit any puckering. The five- and six-membered-ring systems are approximately coplanar (N1–C6, 1.420 (2) Å). The crystal packing, dominated by the O2···H6 intermolecular hydrogen bond (1.87 (2) Å), does not appear to give rise to any noteworthy molecular distortions.[22]

Table I. ^{13}C NMR Spectral Data of **2** in Me_2SO-d_6

structure	carbon	chemical shift, δ obsd[a]	calcd[b,c]	Δ
2a 	a	55.9		
	bb′	117.3	118.5	1.2
	c	123.8	122.5	1.3
	dd′	128.8	128.5	0.3
	e	138.1	139.5	1.4
	f/g	152.3		
		151.0		
2b 	a	56.1		
	b	115.5	116.6	1.1
	c	116.6	118.9	2.3
	d	123.4	122.9	0.5
	e	130.6	129.8	0.8
	f	133.3	134.7	1.4
	g	139.3	140.8	1.5
	h/i	151.0		
		152.5		
2d 	a	13.7		
	b	21.6		
	c	33.1		
	d	34.2		
	e	55.9		
	ff′	117.5	118.5	1.0
	gg′	128.5	128.1	0.4
	h	135.9	136.9	1.0
	i	137.9	138.1	0.2
	j/k	150.9		
		152.2		
2c 	a	56.2		
	bb′	115.0	117.9	2.9
	c	122.8	123.3	0.5
	dd′	134.4	134.7	0.3
	e	142.1	142.1	2.3
	f/g	151.0		
		153.0		

[a] Relative to tetramethylsilane. [b] Reference 18. [c] Reference 19.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer and are calibrated against the 1601-cm^{-1} band of polystyrene. NMR spectra were recorded on a Perkin-Elmer R32 (90 MHz) spectrometer; proton-decoupled carbon-13 NMR spectra were obtained by using dilute deuterated dimethyl sulfoxide solutions on a Varian CFT-20 spectrometer, operating at 20 MHz for carbon-13 and 80 MHz for proton decoupling. Combustion analysis of C, H, and N were performed by SK&F Chemical Analysis Group.

3-[(*p*-*n*-Butylphenyl)amino]-5-methoxy-1,2,4-oxadiazole (1d). 1,2,4-Oxadiazoles **1** were prepared by the general method[15] described previously with some modifications. *N*-(*p*-*n*-butylphenyl)-*N*′-carbmethoxyguanidine (2.49 g, 0.01 mol) was dissolved in 1 N HCl (10 mL), and methylene chloride (30 mL) was added to give a two-phase system. Sodium hypochlorite (6–10 mL of 14% solution) was added to the mixture with stirring at room temperature in the dark. The reaction was followed by TLC until the starting guanidine was depleted. The organic layer was

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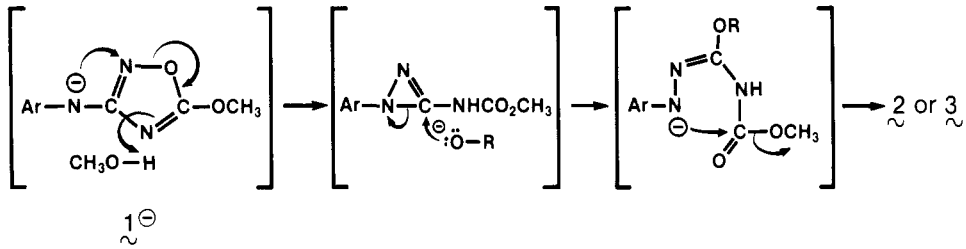
(20) *N*-Aryldiazirines were postulated as intermediates in the photolysis of meso-ionic sydnones, the diazirines subsequently isomerizing to the 1,3-dipolar nitrilimines. C. H. Krauch, J. Kuhls, and H.-J. Piek, *Tetrahedron Lett.*, 4043 (1966); Y. Huseya, A. Chinone, and M. Ohta, *Bull. Chem. Soc. Jpn.* **44**, 1667 (1971); C. S. Angadiyavar and M. V. George, *J. Org. Chem.*, **36**, 1589 (1971); M. Marky, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, *54*, 1275 (1971); H. Gotthardt and F. Reiter, *Tetrahedron Lett.*, 2749 (1971).
(21) G. Ponzio, *Gazz. Chim. Ital.*, **62**, 854 (1932).
(22) A. Rykowski, H. C. van der Plas, and C. H. Stam, *Acta Crystallogr., Sect. B*, **33**, 274 (1977); C. H. Stam and H. C. van der Plas, *ibid.*, **32**, 1288 (1976); P. Prusiner and M. Sundaralingam, *ibid.*, **32**, 419 (1976); A. Kalman, K. Simon, J. Schawartz, and G. Horvath, *J. Chem. Soc., Perkin Trans. 2*, 1849 (1974).

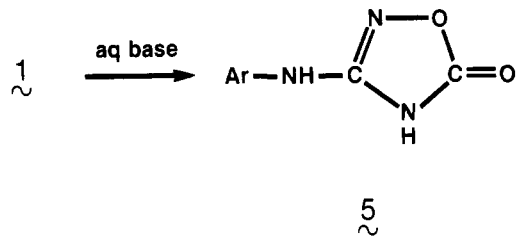
Table II. Yields and Physical Data of 2 and 3

compd	mp, °C	yield, %	anal., % calcd C, H, N	anal., % found C, H, N
2b, $C_9H_8ClN_3O_2$	198–199	82	47.91, 3.57, 18.62	47.74, 3.79, 18.40
2c, $C_9H_7Cl_2N_3O_2$	269–272	95	41.56, 2.71, 16.16	41.77, 2.84, 16.40
2d, $C_{13}H_{17}N_3O_2$	135–138	65	63.14, 6.93, 16.99	63.39, 6.90, 17.36
3a, $C_{10}H_{11}N_3O_2$	148–150	57	58.53, 5.40, 20.48	58.69, 5.82, 20.71
3b, $C_{10}H_{10}ClN_3O_2$	176–178	85	50.12, 4.21, 17.53	49.48, 3.90, 17.73
3c, $C_{10}H_9Cl_2N_3O_2$	241–243	91	43.98, 3.31, 15.33	43.93, 3.14, 15.52

Scheme II



Scheme III



separated and 10% NaOH (20 mL) was added with stirring. The resulting mixture was stirred at room temperature for 1 h, after which the methylene chloride layer was separated, washed with water and saturated NaCl solution, dried ($MgSO_4$), and evaporated to give 2.5 g of solid. Recrystallization from toluene/petroleum ether (bp 35–60 °C) gave 1.8 g (73%) of light-yellow crystals. The product was further purified by column chromatography to give pure white fluffy solid: mp 77–78 °C; mass spectrum (70 eV), 247 (M^+); ^1H NMR ($CDCl_3$) δ 8.10 and 7.05 (ab q, 4), 3.90 (s, 3), 2.55 (t, 2), 1.6–1.0 (m, 7); IR (KBr) 3300, 1595, 1545, 1350 cm^{-1}. Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 63.01; H, 6.86; N, 16.84.

Rearrangement of 1a to 2a in $NaOCH_3/CH_3OH$. A 2.2-g (0.01 mol) sample of 25% sodium methoxide in methanol was added to a 2.0-g (0.01 mol) sample of **1a** in 25 mL of methanol. The resulting solution was heated under reflux for 3 h. The solution was cooled to room temperature and neutralized with 10% HCl. A light-yellow precipitate formed. The precipitate was collected and washed with water. Recrystallization from methanol gave 0.95 g (48%) of white crystals: mp 192–194 °C (lit.[16,17] mp 197, 197–198 °C); mass spectrum (70 eV), 191 (M^+); ^1H NMR (Me_2SO-d_6) δ 7.9–7.1 (m, 5), 3.95 (s, 3); IR (KBr) 3060–2680, 1720, 1660, 1600, 1500, 1340, 1315 cm^{-1}. Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.69; H, 4.94; N, 22.10.

Rearrangements of other oxadiazoles (**1b–1d**) were carried out in similar fashion. The yields, physical properties, and elemental analyses of **2** and **3** are listed in Table II.

Base Hydrolysis of 1a to 5. To 0.2 g (1.0 mmol) of **1a** in 5 mL of methanol was added 1.5 mL of 20% aqueous NaOH. The mixture was heated to reflux for 45 min. After cooling to room temperature the mixture was quenched with 5 mL of 10% HCl. A fine white powder precipitated from solution. Recrystallization from $MeOH/H_2O$ (1:1, v/v) gave 0.13 g (0.74 mmol; 74%), mp 186–187 °C dec. Anal. Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.95; N, 23.73. Found: C, 54.78; H, 3.90; N, 24.50.

X-ray Data Collection.[23] Full details of the X-ray data collection and structure solution and refinement are available.

(23) Molecular structures Corporation, College Station, TX.

(See paragraph at the end of paper about supplementary material.)

Acknowledgment. Spectral measurements by SK&F Chemical Analysis Group are gratefully appreciated. We thank Dr. I. J. Turchi, Dr. C. E. Berkoff, and Dr. R. L. Webb for many helpful discussions.

Registry No. 1a, 58598-94-0; **1b**, 58599-07-8; **1c**, 59496-76-3; **1d**, 81012-74-0; **2a**, 14500-22-2; **2b**, 81012-75-1; **2c**, 81012-76-2; **2d**, 81012-77-3; **3a**, 14495-36-4; **3b**, 81012-78-4; **3c**, 81012-79-5; **5**, 81012-80-8; *N*-(*p*-*n*-butylphenyl)-*N'*-carbmethoxyguanidine, 81012-81-9.

Supplementary Material Available: X-ray data collection, structure solution and refinement description; tables for crystal data, least-squares plane calculations, intramolecular bond distances and angles, and atomic coordinates (8 pages). Ordering information is given on any current masthead page.

Structure of 2-Acetyl-6-(dimethylamino)fulvene and Its Reactions with Primary and Secondary Amines[1]

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Received September 9, 1981

In connection with studies on derivatives of cyclopenta[*d*]pyridazines[2] it was desired to prepare 2-acetyl-6-(dimethylamino)fulvene (**3**) as a possible intermediate to 1-methyl derivatives and examine its reactions with primary and secondary amines. Fijisawa and Sakai[3] had reported the synthesis of **3** by (i) the acetylation of sodium cyclopentadienide with ethyl acetate to form acetylcyclopentadiene **1**, (ii) treatment of **1** with 1 equiv of ethoxide to form **2**, and (iii) reaction of **2** with dimethylformamide, phosphorus oxychloride, and 3 equiv of methoxide. In our hands acetyl chloride was a better acetylation reagent, and the generation of **2** with 1 equiv of methoxide followed by treatment with the Vilsmeier reagent from dimethylform-

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