reaction of benzaldehyde with *tert*-butyl 2-bromothiolpropionate (**1b**) using the NaH-DMF conditions, the trans isomer predominated, although the cis thiolglycidate was favored in the reaction of *tert*-butyl 2-bromothiolacetate (**1a**) with benzaldehyde under the same conditions. Although the explanation for this result is not immediately apparent, the high percentage of the trans isomer obtained in the less polar THF solvent in the reaction of benzaldehyde with *tert*-butyl 2-bromothiolacetate (**1a**) could be explained on the basis of steric considerations assuming that the last, intramolecular substitution step in the reaction is rate limiting.[7] We are continuing our studies with glycidic thiol esters in an attempt to determine the origin of these unusual stereochemical results.

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References and Notes

(1) Presented in part at the 6th Central Regional Meeting of the American Chemical Society, Detroit, Mich., April 21-24, 1974.

(2) For reviews of thiol ester chemistry, see T. C. Bruice in "The Chemistry of Organic Sulfur Compounds," Vol. 1, Pergamon Press, Oxford, 1961, p 421; M. J. Janssen in "The Chemistry of Functional Groups—The Chemistry of Carboxylic Acids and Esters," Interscience, London, 1969, p 724.

(3) J. Wemple, *J. Amer. Chem. Soc.*, **92**, 6694 (1970).

(4) An unsuccessful attempt has been reported: L. Field and C. G. Carlile, *J. Org. Chem.*, **26**, 3170 (1961).

(5) Protic solvents (alcohols) and nucleophilic (NaOEt) bases have been generally used in the Darzens reaction in the synthesis of epoxides substituted with a wide variety of electron-withdrawing groups. For example, aqueous methanolic NaOH has been used recently in the Darzens condensation of 1-chloro-3-diazopropanone with benzaldehyde: N. F. Woolsey and M. H. Khalil, *J. Org. Chem.*, **38**, 4216 (1973).

(6) M. S. Newman and B. J. Magerlein, *Org. React.*, **5**, 417 (1949). However, α-bromo esters have recently been shown to be preferred to α-chloro esters in the synthesis of glycidic esters from low molecular weight aldehydes such as acetaldehyde.[7]

(7) R. F. Borch, *Tetrahedron Lett.*, 3761 (1972).

(8) *tert*-Butyl 2-bromothiolacetate was obtained from bromoacetyl bromide, *tert*-butyl mercaptan, and pyridine as a colorless oil: n^{26}_{D} 1.5077; nmr (CCl$_4$, TMS) δ 3.88 (s, 2 H), 1.48 (s, 9 H); ir (thin film) 1690 cm^{-1}.

(9) The epoxide proton coupling constants are in agreement with the trans (1.5 Hz) and cis (4.5 Hz) stereochemical assignments: R. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Amer. Chem. Soc.*, **80**, 6389 (1958).

(10) n^{26}_{D} 1.4965; nmr (CCl$_4$, TMS) δ 4.31 (q, 1 H, J = 7.0 Hz), 1.77 (d, 3 H, J = 7.0 Hz), 1.48 (s, 9 H); ir (thin film) 1690 cm^{-1}.

(11) Ethyl (*E*)-2-methyl-3-phenyloxiranecarboxylate was prepared according to the method of V. R. Valente and J. L. Wolfhagen, *J. Org. Chem.*, **31**, 2509 (1966). It was hydrolyzed with NaOH in ethanol to give the corresponding sodium salt.

(12) The trans isomer also predominated (90% trans, 10% cis) in the reaction of benzaldehyde and *tert*-butyl 2-bromothiolbutyrate with NaH in DMF. It is interesting to note that in both cases the small amount of cis isomer was easily removed by short-path distillation at ~130°.

(13) See F. W. Bachelor and R. K. Bansal, *J. Org. Chem.*, **34**, 3600 (1969), and references cited therein.

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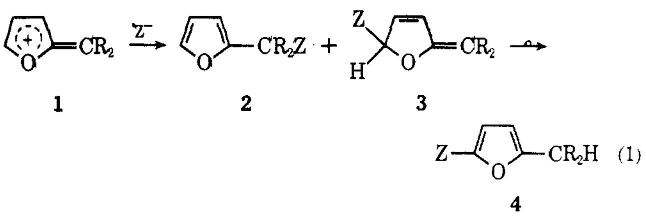
Furfuryl Cationic Capture Processes. 5-Substituted $\Delta^{3,4}$-2,5-Dihydro-2-methylenefurans and Their Rearrangement to Furfuryl Derivatives

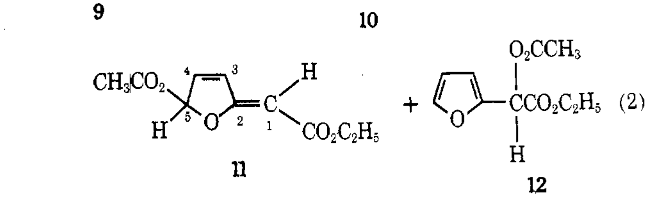
Summary: Decomposition of ethyl (2-furyl)diazoacetate (**9**) occurs carbenically to **17** and cationically by 1,1 and 1,5 solvent incorporation to derivatives of **2** and **3**; ring closures of **17** by hydroxylic solvents as catalyzed by silver(I) yield furans **3** which isomerize anionotropically to **2**.

Sir: Furfuryl cations (**1**) usually undergo nucleophilic conversion to furfuryl analogs (**2**, eq 1).[1a] Such cations (**1**) might also be expected to react at their 5 positions to give $\Delta^{3,4}$-2-alkylidene-2,5-dihydrofurans (**3**, eq 1) which tautomerize to 5-substituted 2-alkylfurans (**4**, eq 1).[1b-d,2] As yet, however, products analogous to **3** have been detected only in reaction of 2-furyldiphenylcarbinol (**5**) with methanolic hydrochloric acid to give $\Delta^{3,4}$-2-diphenylmethylidene-5-methoxy-2,5-dihydrofuran (**6**) and methyl 2-furyldiphenylcarbinyl ether (**7**).[3] Methanolic hydrochloric acid then effects prototropic rearrangement of **7** to 2-diphenylmethyl-5-methoxyfuran (**8**).[3]



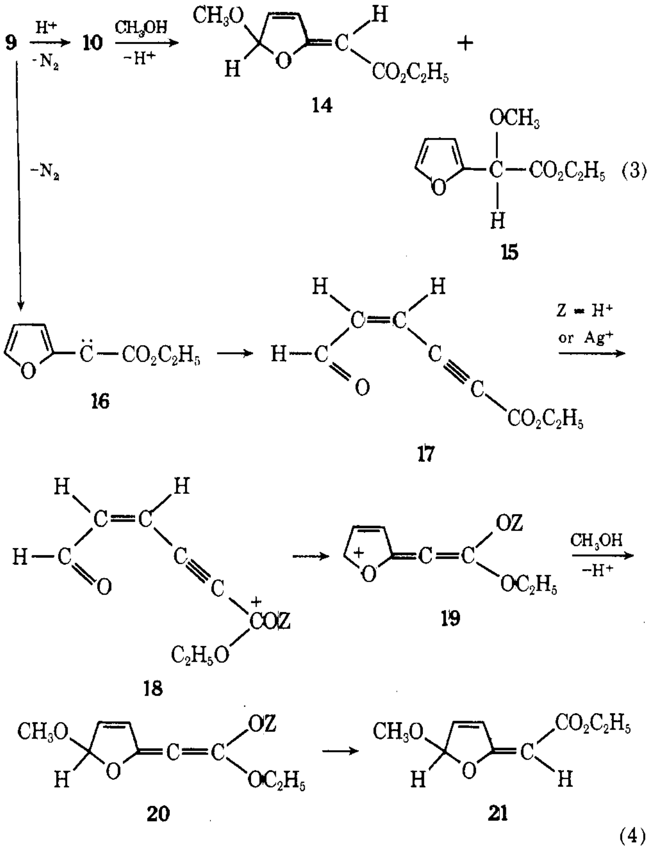
We now report a series of cationic reactions of ethyl (2-furyl)diazoacetate (**9**) in which nucleophiles are incorporated at the 5-furano position (as **3** in eq 1); these products may then undergo anionotropic isomerization to ethyl α-substituted α-(2-furyl)acetates (**2**, eq 1) rather than tautomerization to ethyl (5-substituted 2-furyl)acetates (**4**, eq 1). Of further significance are that cationic conversion of **9** by nucleophiles may be directed to **2** or **3** by appropriate catalysts and that carbenic decomposition of **9** (eq 3) and subsequent reaction with hydroxylic solvents (eq 4) serves as a new method for synthesis of derivatives such as **3**.

Diazo ester **9**, prepared from ethyl (2-furyl)glyoxylate *p*-tosylhydrazone and tetramethylguanidine, reacts with acetic acid (eq 2) at 25° to give (*Z*)-$\Delta^{3,4}$-5-acetoxy-2-carboethoxymethylidene-2,5-dihydrofuran (**11**, 55%) and ethyl α-acetoxy-α-(2-furyl)acetate (**12**, 45%).[4] Esters **11** and **12** are apparently produced by reactions of acetic acid with α-carboethoxyfurfuryl carbenium ion **10** at its 5-furano and its furfuryl positions, respectively. It is not clear whether reaction to give **11** and **12** occurs by protonation of **9** or/and its subsequent carbene (**16**). The stereochemistry of **11** is assigned on the basis that it is not isomerized when heated and the supposition that the steric bulk about furano oxygen is less than that at C-3 H.



Isomerization of **11** occurs in acetic acid at 85° to give **12**; prototropic rearrangement of **11** to ethyl α-(5-acetoxy-2-furyl)acetate (**13**) does not take place. Reaction of **9** with acetic acid thus reveals that 1,5-cationic addition to give **11** is the major kinetic process, whereas **12**, formally the product of 1,1-cationic addition of acetic acid to **9**, may result from thermodynamic or kinetic circumstances. The present observations raise the possibility that solvolysis of furfuryl derivatives to furfuryl analogs (eq 1) may be more complex than has been apparent.

A study has also been made of reactions of **9** with alcohols. Thus **9** decomposes in methanol with nitrogen evolution to (*Z*)-$\Delta^{3,4}$-2-carboethoxymethylidene-5-methoxy-2,5-dihydrofuran[4] (**14**, 29%, eq 3) and ethyl α-methoxy-α-(2-furyl)acetate[4] (**15**, 17%, eq 3) along with ethyl 5-formyl-*cis*-



4-penten-2-ynoate[4] (**17**, 34%, eq 4) and (E-$\Delta^{3,4}$-2-carboethoxymethylidene-5-methoxy-2,5-dihydrofuran[4] (**21**, 21%, eq 4). Esters **14** and **15** are presumably formed by attack of methanol on **10** (Eq 3). Aldehydo ester **17** is a product of carbenic reaction[5] of **9** (eq 4) even though the environment is protic. Indeed decomposition of **9** in methylene chloride results in evolution of nitrogen and stereospecific conversion to **17** (100%, eq 4).[5] The conclusion that **9** undergoes competitive carbenic decomposition in methanol is consistent with the observation that upon addition of *p*-toluenesulfonic acid (0.5 equiv) the conversions to **14** (44%) and **15** (16%) are increased.

Of particular note is that **17** reacts with methanol as catalyzed by protonic acids or much faster and more efficiently (100%) by silver nitrate to give **21**, the E isomer of **14**. Conversion of **17** to **21** is a new synthesis of $\Delta^{3,4}$-2-alkylidene-2,5-dihydrofurans and may be the source of **21** obtained from **9** and methanol *via* a mechanistic sequence as in eq 4. The stereochemistry of **21** is presumed on the basis that protic attack is favored kinetically from the furano oxygen direction in **20** and in particular that **21** is converted by heat or by uv irradiation to its less strained isomer **14**.

Silver nitrate in methanol converts **9** rapidly to **14** (25%), **15** (11%), and **21** (65%), presumably by processes analogous to those of eq 3 and 4. Of interest is that cupric acetate reacts rapidly with **9** and methanol exclusively by 1,1 addition (100%) to give **15**. The present example of 1,1 rather than 1,5 addition of methanol to **9** with loss of nitrogen emphasizes further the specificity possibly derived from reactions of diazo compounds as catalyzed by copper ions.[6]

Acknowledgment. We gratefully acknowledge the National Science Foundation and the National Institutes of Health for support of this research.

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