

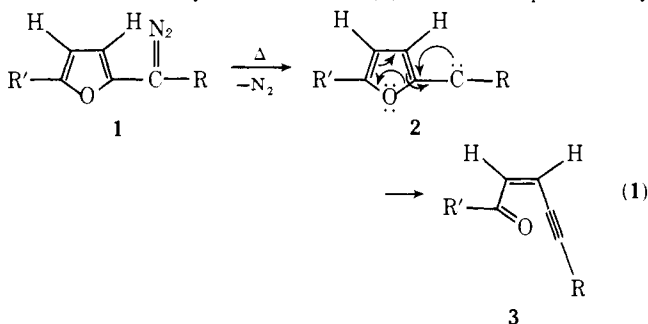
# Carbenic, Cationic, Metal Ion Catalyzed, and Photolytic Decompositions of Ethyl (2-Furyl)diazoacetate<sup>1</sup>

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**Abstract:** Ethyl (2-furyl)diazoacetate (**4**) decomposes carbenically with loss of nitrogen and collapse of its furan ring to give ethyl 5-formyl-*cis*-4-penten-2-ynoate (**6**). Cationic decomposition of **4** occurs in acetic acid with nitrogen evolution but without ring cleavage to yield (*Z*)- $\Delta^{3,4}$ -5-acetoxy-2-carboethoxymethylidene-2,5-dihydrofuran (**9**) and ethyl  $\alpha$ -acetoxy- $\alpha$ -(2-furyl)acetate (**10**) by overall 1,5- and 1,1-addition processes, respectively, of kinetic control. Dihydrofuran **9** isomerizes in hot acetic acid to **10**; prototropic isomerization of **9** to ethyl  $\alpha$ -(5-acetoxy-2-furyl)acetate (**14**) does not occur. In alcohols, solvents of lower protic capacity than carboxylic acids, competitive cationic and carbenic reactions of **4** result in ethyl  $\alpha$ -alkoxy- $\alpha$ -(2-furyl)acetates, (*Z*)-5-alkoxy- $\Delta^{3,4}$ -2-carboethoxymethylidene-2,5-dihydrofurans, and **6**; acid-catalyzed ring closures of **6** by the alcohols also give (*E*)-5-alkoxy- $\Delta^{3,4}$ -2-carboethoxymethylidene-2,5-dihydrofurans competitively. Copper reagents in alcohols effect accelerated decomposition of **4** with 1,1 (major) and 1,5 incorporation of the alcohols. Silver ion in alcohols also catalyzes decomposition of **4**; the overall processes, however, are similar to those in the absence of silver(I). Photosensitized, photolytic, and thermal decompositions of **4** in alcohols give identical overall carbenic and cationic products. These reactions of **4** appear to involve (eventually) singlet carboethoxy(2-furyl)methylene (**5**) which is then partitioned by competitive carbenic and cationic processes.

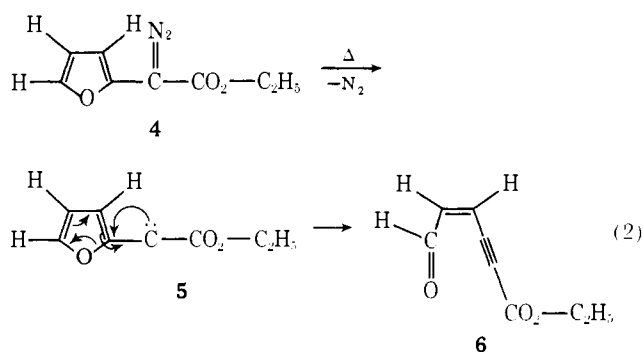
Thermolysis of 1-diazo-1-(2-furyl)alkanes (**1**, eq 1) results in loss of nitrogen and electrocyclic ring opening of the intermediate furfurylidene (**2**) to give *cis*- $\gamma,\delta$ -acetylenic  $\alpha,\beta$ -olefinic aldehydes and ketones (**3**).<sup>2</sup> We now report a study



of carbenic, cationic, metal ion catalyzed, and photolytic decompositions of ethyl (2-furyl)diazoacetate (**4**). The investigation reveals that (1) **4** decomposes carbenically with collapse of its furan ring, (2) kinetic control in cationic decomposition of **4** as effected by protic reagents results in nitrogen loss and overall 1,1- and 1,5-addition, (3) silver and copper ions catalyze decomposition of **4** in nucleophilic environments by greatly different processes, (4) thermolysis, photolysis, and photosensitization of **4** in alcohols eventually involve the same mechanistic intermediates, and (5) appropriate control of various carbenic and carbenium ion reactions of **4** leads to efficient and novel synthetic methods.

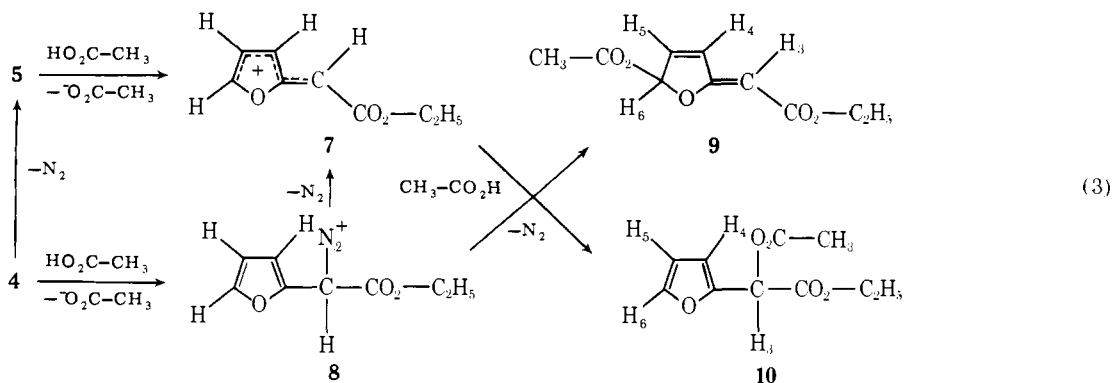
## Results and Discussion

$\alpha$ -Diazo ester **4**, conveniently prepared (66%) from ethyl (2-furyl)glyoxylate 2,4,6-trimethylbenzenesulfonylhydrazone<sup>3</sup> and tetramethylguanidine (1 equiv)<sup>4</sup> at 20–25 °C, is a red solid, mp 25 °C, that is storable at –25 °C without change. Upon warming neat to room temperature, in solution in dichloromethane for less than 8 h, or upon vacuum evaporation through a heated tube (250 °C), **4** decomposes with evolution of nitrogen and ring opening to give ethyl 5-formyl-*cis*-4-penten-2-ynoate (**6**, eq 2) in excellent yields (~100%). The carbenic behavior of **5** is thus analogous to that of **2**.<sup>2</sup> Aldo ester **6** is a clear liquid that is stable indefinitely at 0 °C, decomposes slightly at 25 °C, but resinifies when heated or upon gas chromatography. The stereochemistry of **6** is shown to be *cis* by its vinyl coupling constant of 11 Hz<sup>5</sup> and the absence of trans-olefin IR stretching.<sup>6</sup>



Diazo ester **4** (Table I) was then decomposed in acidic environments to determine its various cationic products. Acetic acid reacts with **4** at 25 °C with nitrogen evolution and without ring cleavage to yield (*Z*)- $\Delta^{3,4}$ -5-acetoxy-2-carboethoxymethylidene-2,5-dihydrofuran (**9**, 46%) and ethyl  $\alpha$ -acetoxy- $\alpha$ -(2-furyl)acetate (**10**, 54%)<sup>7</sup> as summarized in eq 3. Upon dilution of the acetic acid with ethyl ether or dichloromethane, **4** undergoes ring opening to **6** (36 and 16%, respectively) along with conversion to **9** and **10**.<sup>7</sup> The structures of **9** and **10** are assigned by IR, mass spectral, and NMR methods. The stereochemistry of **9** as the *Z* rather than the *E* isomer is presumptive; the adduct is not discernibly isomerized about its 2-carboethoxymethylidene moiety in hot acetic acid, and it is supposed that the steric strain within the  $\alpha$ -carboethoxymethylidene moiety is less when syn to furano oxygen than to H<sub>4</sub>.

The conversion of **4** by acetic acid to **9** and **10** apparently involves nucleophilic attack of the carboxylic acid on the  $\alpha$ -carboethoxyfurfurylcarbenium ion (**7**) and/or possibly the  $\alpha$ -carboethoxyfurfuryldiazonium ion (**8**) at their 5-furano and their furfuryl positions (eq 3). The precise mechanistic details for these cationic processes have not been finally delineated<sup>7</sup> but there is substantial evidence that an important source of carbenium ion **7** is protonation of singlet carboethoxy(2-furyl)methylene (**5**, eq 3). When the acetic acid is diluted with ethyl ether or dichloromethane, carbenic collapse of **4** via **5** to **6** (Table I) becomes competitive with the reactions yielding **9** and **10**.<sup>8</sup> Conversions of **4** via **7** to **9** and **10** by 1,5 and 1,1 incorporation of acetic acid are formally analogous to reactions of 2-furyldiphenylcarbinol (**11**) with methanolic hydrochloric acid to give  $\Delta^{3,4}$ -diphenylmethylidene-5-methoxy-2,5-dihy-



**Table I.** Decomposition of Ethyl (2-Furyl)diazoacetate (**4**) in Hydroxylic Solvents<sup>a</sup>

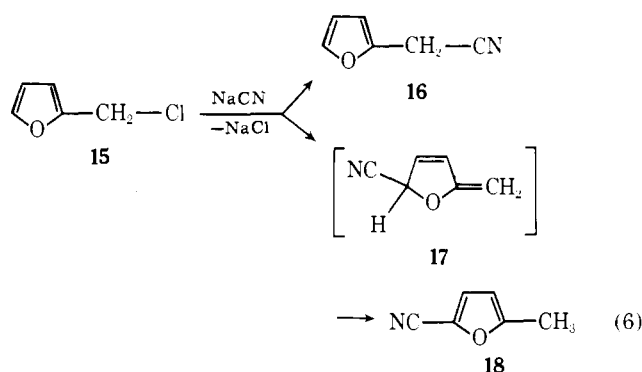
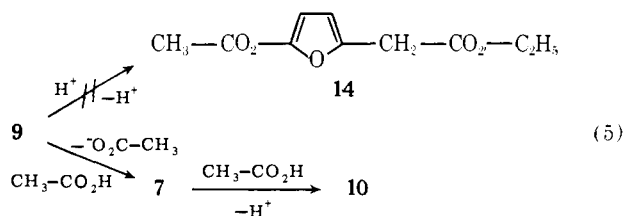
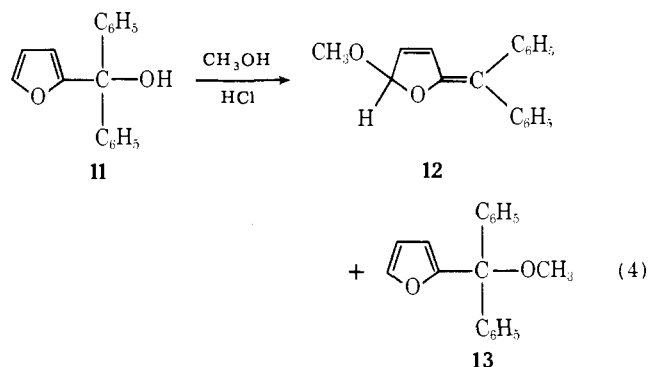
reagent	temp, °C	time, h	product distribution (%)
CH <sub>3</sub> CO <sub>2</sub> H	25	4	<b>9a</b> (54), <b>10a</b> (46)
CH <sub>3</sub> CO <sub>2</sub> H/ (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O	25	5	<b>6</b> (36), <b>9</b> (12), <b>10</b> (52)
CH <sub>3</sub> CO <sub>2</sub> H/CH <sub>2</sub> Cl <sub>2</sub>	25	5	<b>6</b> (20), <b>9</b> (23), <b>10</b> (57)
CH <sub>3</sub> OH	25	3	<b>6</b> (34), <b>19a</b> (15), <b>20a</b> (29), <b>24a</b> (21)
CH <sub>3</sub> OH	-25	1440	<b>6</b> (26), <b>19a</b> (15), <b>20a</b> (28), <b>24a</b> (31)
CH <sub>3</sub> OH	60	0.25	<b>6</b> (42), <b>19a</b> (15), <b>20a</b> (30), <b>24a</b> (13)
CH <sub>3</sub> OH/TsOH <sup>b</sup>	25	0.75	<b>19a</b> (16), <b>20a</b> (44), <b>24a</b> (40)
CH <sub>3</sub> CH <sub>2</sub> OH	25	12	<b>6</b> (64), <b>19b</b> (12), <b>20b</b> (24)
CH <sub>3</sub> CH <sub>2</sub> OH/TFA <sup>c</sup>	25	4	<b>6</b> (22), <b>19b</b> (16), <b>20b</b> (46), <b>24b</b> (15)
(CH <sub>3</sub> ) <sub>2</sub> CHOH	25	5	<b>6</b> (>95), <b>19c</b> (tr), <sup>d</sup> <b>20c</b> (tr)
(CH <sub>3</sub> ) <sub>2</sub> CHOH/ TsOH <sup>b</sup>	25	2	<b>19c</b> (7), <b>20c</b> (53), <b>24c</b> (40)

<sup>a</sup> The results summarized are the averages of two or more experiments. In general these experiments are quite reproducible and the yields approach 100%. <sup>b</sup> *p*-Toluenesulfonic acid <sup>c</sup> Trifluoroacetic acid. <sup>d</sup> tr = trace.

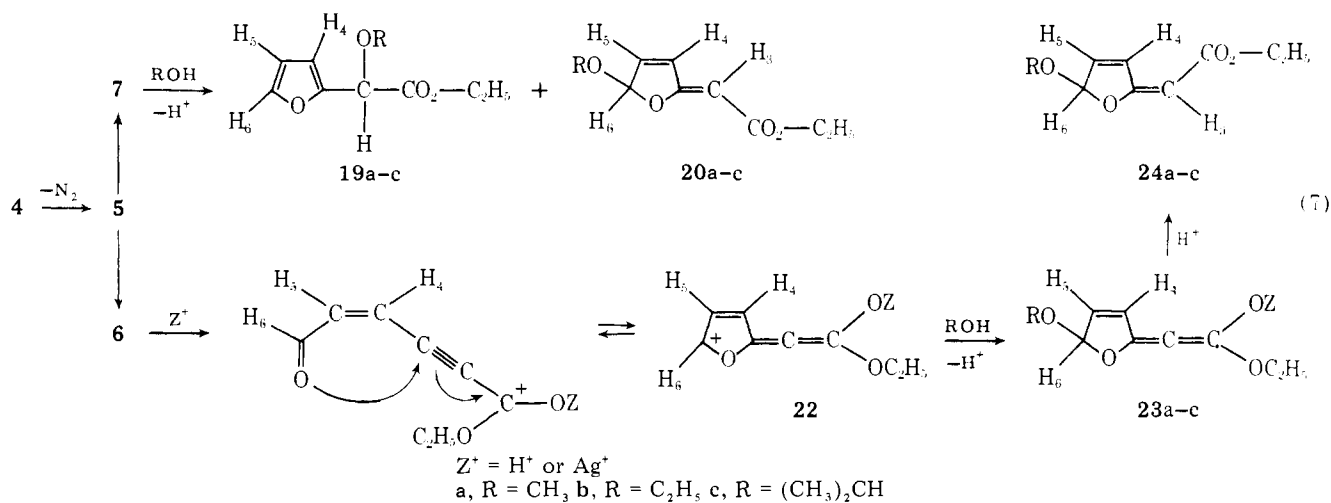
dofuran (**12**) and methyl 2-furyldiphenylcarbinyl ether (**13**).<sup>9,10</sup>

Dihydrofuran **9** is thermally labile. In acetic acid at 85 °C, **9** undergoes slow rearrangement of its acetoxy group to give its 1,1 isomer **10** (76%), presumably via carbenium ion **7** (eq 5); prototropic isomerization of **9** to ethyl  $\alpha$ -(5-acetoxy-2-furyl)acetate (**14**, eq 5) does not occur and **10** is not detectably converted to **9** by warm glacial acetic acid. Acetate **10** is thus thermodynamically more stable than **9** and conversion of **4** by acetic acid to **9** is a process of kinetic control. Furfuryl systems have been previously observed to undergo S<sub>N</sub>2 displacement and then tautomerism to 5-substituted furan derivatives **10**.<sup>11</sup> For example, furfuryl chloride (**15**) is converted (eq 6) by sodium cyanide to 5-cyano-2-methylfuran (**16**) and (2-furyl)acetonitrile (**18**);<sup>11</sup> **18** presumably arises by prototropy of  $\Delta^{3,4}$ -5-cyano-2-methylene-2,5-dihydrofuran (**17**). The present conversions of **4** by acetic acid to **9** and **10** and then anionotropic rearrangement of **9** to **10** reveal the subtleties of kinetic and thermodynamic capture reactions of carbenium ion **8**. Such processes for other furfurylcarbenium ion intermediates may be more prevalent than presently recognized.

It was then of interest to study decomposition of **4** in solvents of lower protic capacity than carboxylic acids and thus the reactions of **4** in the presence of various alcohols were investigated (Table I). In methanol at 25 °C, **4** is slowly converted (eq 7) to ethyl  $\alpha$ -(2-furyl)- $\alpha$ -methoxyacetate (**19a**, 17%) and



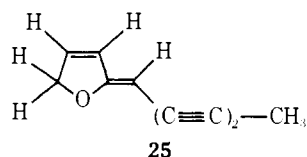
(*Z*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-methoxy-2,5-dihydrofuran (**20a**, 29%) along with **6** (34%) and (*E*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-methoxy-2,5-dihydrofuran (**24a**, 21%). Analogues corresponding to **24a** were not observed in reactions of **4** with acetic acid. The decomposition of **4** in methanol containing *p*-toluenesulfonic acid differs further (Table I) in that conversions to **20a** (44%) and **24a** (40%) are increased relative to **19a** (16%), and **6** is absent. Of significance because it is a new synthetic method for preparing 2,5-dihydrofuran derivatives and because of its mechanistic implication with respect to the overall behavior of **4** is that **6** is converted to a 35:65 mixture of **24a** and **6** upon storage in methanol for 12 h. Neither **19a** nor **20a** is observed and **19a** and **20a** neither interconvert nor give **24a** under these conditions. These experiments establish that **19a** and **20a** are the primary protic products of reaction of **4** with methanol possibly via **5** and that **24a** is a secondary product derived from **6**. Further, conversion of **6** to **24a** in methanol occurs rapidly and quantitatively upon



addition of traces of silver nitrate and thus is the synthetic method of choice for **24a**.

The structure of **19a** is established by its NMR for furan ring protons at  $\delta$  6.39 (s, 2 H) and 7.48 (s, 1 H), respectively, and UV absorption at  $\lambda_{\max}$  220 nm ( $\epsilon$  6300).<sup>6</sup> The NMR of the  $\alpha$ -methyne proton ( $H_3$ ) in **19a** is a sharp singlet at  $\delta$  4.85 and the composition of **19a** in admixture with **6**, **20a**, and **24a** is obtained readily by integration of this signal.

Assignment of **20a** is based on its spectral properties. The dihydrofuran (**20a**) is of proper mass, has strong IR absorption at  $5.95 \mu$  indicative of the conjugated unsaturated ester function, and exhibits UV absorption at  $\lambda_{\max}$  278 nm ( $\epsilon$  12 000), calcd 278 nm.<sup>12</sup> The NMR of **20a** reveals vinyl resonances at  $\delta$  7.38 (d,  $H_4$ ,  $-\text{CH}=\text{C}<$ ) and 6.26 (split d,  $H_5$ ,  $-\text{C}=\text{CH}-$ ,  $J_{5,6} = 1$  Hz) with *vicinal* coupling of 6 Hz and absorptions at  $\delta$  5.20 (s,  $H_3$ ,  $-\text{C}=\text{CHCO}_2-$ ,  $J_{3,4} = 0.5$  Hz) and 5.76 (s,  $H_6$ ,  $\text{ROCHO}$ ).<sup>13</sup> The assignments of  $H_3$  and  $H_6$  as singlets are confirmed on the basis that monodeuterated **20a**, obtained by decomposing **4** in methanol-*O-d*, lacks a singlet absorption at  $\delta$  5.20 but its NMR is identical in all other respects with that of **20a**.<sup>13</sup> The exocyclic carbon-carbon double bond of **20a** is assigned the *Z* configuration on the basis that **24a** is isomerized to **20a** by heat or UV irradiation, **25** exists preferentially in the



*Z* configuration,<sup>14</sup> and intuitively that **20a** is less strained than **24a**.

The IR and UV spectra of **24a** are consistent with its conjugatively diunsaturated ester assignment and are essentially identical with those of **20a**. The NMR spectrum of **24a** is different from **20a** and reveals two unresolved protons at  $\delta$  6.20 (br s,  $H_4$ ,  $-\text{CH}=\text{C}<$  and  $H_5$ ,  $-\text{C}=\text{CH}<$ ) and singlets at  $\delta$  4.78 ( $H_3$ ,  $-\text{C}=\text{CHCO}_2-$ ) and 5.96 ( $H_6$ ,  $\text{ROCHO}$ ), respectively. The shielding of  $H_5$  in **24a** relative to **20a** presumably arises from the steric crowding between  $H_4$  and the carboethoxy group which leads to diminished conjugation with the heterocyclic  $\pi$  system and thus increased electron density at the  $\delta$  position. The NMR of monodeuterated **24a**, prepared by cyclization of **6** in methanol-*O-d*, lacks the  $H_3$  singlet at  $\delta$  4.78 but other than that is identical with that of **20a**. The complete conversion of **24a** to **20a** upon gas chromatography is indicative of the greater thermodynamic stability of **20a**.<sup>15</sup>

Reactions of **4** to give **19a** and **20a** apparently result from cationic exchange of **7** (and/or **8**) with methanol<sup>16</sup> (eq 7). Aldehyde ester **6** is formed by carbenic decomposition of **4** even though the reaction medium is protic.<sup>16</sup> The increased con-

versions of **4** to **19a** and **20a** by methanol upon addition of *p*-toluenesulfonic acid are consistent with the gross interpretation of competitive cationic and carbenic reaction processes in eq 7. Temperatures ranging from  $-25$  to  $60^\circ\text{C}$  have only minor relative effects on the competitive decomposition reactions of **4**. Presumably the **24a** from **4** and methanol arises from acid-catalyzed ring closure of **6** and addition of the alcohol (eq 7). Formation of **24a** rather than **20a** possibly results from kinetic control in tautomerism of **23a** in which entry of the proton is favored from the furano oxygen direction.

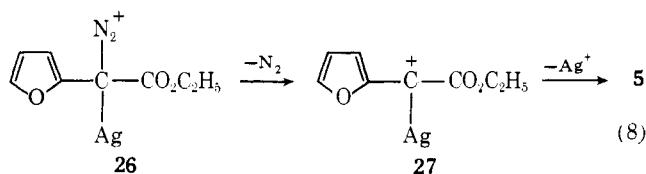
The reactions of **4** with other alcohols were also investigated (Table I). Ethanol converts **4** at  $25^\circ\text{C}$  to **6** (64%), ethyl  $\alpha$ -ethoxy- $\alpha$ -(2-furyl)acetate (**19b**, 12%), and (*Z*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-ethoxy-2,5-dihydrofuran (**20b**, 24%). In 2-propanol **4** collapses almost completely carbenically (>95%) to **6**; only traces of ethyl  $\alpha$ -(2-furyl)- $\alpha$ -(2-propoxy)acetate (**20c**) and (*Z*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-(2-propoxy)-2,5-dihydrofuran (**20c**) are formed. The yields of solvent incorporation products from **4** and alcohols increase in the order 2-propanol (<5%), ethanol (36%), and methanol (45%) and thus parallel the acidity order of the alcohols.<sup>17</sup> Solvent incorporation by cationic capture of **7** and/or **8** and by reactions with **6** are increased upon decomposition of **4** by alcohols in the presence of stronger acids. Thus **4**, ethanol, and trifluoroacetic acid (Table I) yield **6** (22%), **19b** (16%), **20b** (46%), and (*E*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-ethoxy-2,5-dihydrofuran (**24b**, 15%); **4**, 2-propanol, and *p*-toluenesulfonic acid form **19c** (7%), **20c** (53%), and (*E*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-(2-propoxy)-2,5-dihydrofuran (**24c**, 40%). As expected, **6** is converted rapidly by ethanol and by 2-propanol, upon addition of silver nitrate, to **24b** and **24c**, respectively, which then isomerize completely to **20b** and **20c** upon gas chromatography.

Silver and copper ions dramatically speed decomposition of **4**. When **4** is treated with methanol containing small amounts of silver nitrate, vigorous exothermic processes occur with nitrogen evolution (Table II) to yield **19a** (11%), **20a** (25%), and **24a** (65%). Reactions of **9** with 2-propanol/silver nitrate (Table II) give **19c** (trace), **20c** (23%), and **24c** (78%). On the basis that the **24a** obtained from **4**, methanol, and silver nitrate is formed by reaction of **6** with methanol, the ratios of ring opening to primary cationic incorporation of methanol by **4** in the presence and in the absence of silver ion are quite similar. Such behavior is also the case in the reactions of **4** with 2-propanol in the presence or absence of silver nitrate. The spectacular catalytic effect of silver ion<sup>18</sup> on **4** may involve formation of silver-cationic intermediates such as **26** and/or **27** which then (1) lose (nitrogen and) silver ion and convert to carbene **5** (eq 8) and its products, and (2) to a lesser extent, undergo electrophilic capture of the alcohols via overall processes as in eq 7.

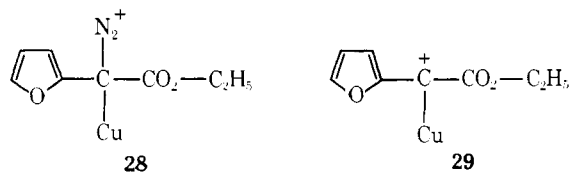
**Table II.** Metal Ion Catalyzed Decompositions of Ethyl (2-Furyl)diazoacetate (**4**) in Methanol

reagent <sup>a</sup>	time, h	product distribution, %			
		<b>6</b>	<b>19a</b>	<b>20a</b>	<b>24a</b>
AgNO <sub>3</sub> <sup>b</sup>	1		11	25	65
CuCl <sup>b</sup>	1		75	25	
CuCl <sub>2</sub> <sup>b</sup>	1		>95		tr <sup>d</sup>
Cu(NO <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	1		>95	tr <sup>d</sup>	
Cu(OAc) <sub>2</sub> <sup>b</sup>	1		>95	tr <sup>d</sup>	
HgCl <sub>4</sub> <sup>b</sup>	30		10	55	35
Rh <sub>2</sub> Cl <sub>2</sub> (CO) <sub>4</sub> <sup>c</sup>	10		39	37	24
Ca(NH <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> <sup>c</sup>	210		19	48	33
Fe(NH <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub> <sup>c</sup>	120	25	36	27	12
Co(OAc) <sub>2</sub> ·3H <sub>2</sub> O <sup>c</sup>	120	28	15	34	22
NiCl <sub>2</sub> <sup>c</sup>	120	32	18	32	18
Ca(OAc) <sub>2</sub> ·H <sub>2</sub> O <sup>c</sup>	120	14	14	40	32
Zn(OAc) <sub>2</sub> <sup>c</sup>	120	29	14	33	24
Pb(OAc) <sub>2</sub> <sup>c</sup>	120	20	16	32	25
Hg(OAc) <sub>2</sub> <sup>c</sup>	90	34	16	34	16
Tl(O <sub>2</sub> CCF <sub>3</sub> ) <sub>3</sub> <sup>c</sup>	90	32	19	34	15
Pd, C <sup>c</sup>	120	33	19	32	16
powdered glass <sup>c</sup>	120		15	36	48

<sup>a</sup> The reaction mixtures consisted of 0.5 mmol of **4**, 4 mL of methanol, and 10 mg of metal salt. <sup>b</sup> The yields in these experiments are essentially 100%. <sup>c</sup> The yields range from 65 to 85%. <sup>d</sup> tr = trace.



Various copper reagents catalyze decomposition of **4**.<sup>19</sup> Nitrogen evolution is complete in less than 1 min when **4** in methanol is treated with cuprous chloride, cupric nitrate, or cupric acetate. NMR analysis of the product as obtained by catalysis with the various Cu<sup>II</sup> salts shows that only 1,1-addition to give **19a** occurs (Table II). The Cu<sup>I</sup> salt, cuprous chloride, leads primarily to 1,1-addition to form **19a** (75%); 1,5-addition to **4** yielding **20a** is a minor process (25%). Ring opening to **6** is not observed in these experiments, and furthermore **6** is unchanged when treated with the copper reagents, thus ruling out its conversion to **19a** under the conditions for copper-catalyzed decomposition of **4**. Silver and copper ions exhibit great catalytic activities for decomposing **4** but there are enormous differences in the reaction products. The cupric (or cuprous) ion, possibly upon coordination with **4** as in **28** and/or **29**, allows mainly 1,1-addition whereas silver



ion (possibly a better leaving ion) results in major collapse to **6** (Eq 8). The present observation of 1,1- rather than 1,5-addition of methanol to **4** with loss of nitrogen is another impressive example of the specificity obtainable from diazo compounds in reactions catalyzed by copper ions.<sup>20</sup>

Chloroauric acid and rhodium dicarbonyl dimer have moderate catalytic activities for decomposing **4**. The reactions do not show marked specificity since **19a**, **23a**, and **24a** are all formed in significant quantities (Table II). A wide variety of metal salts have also been tested as catalysts for **4** (Table II). In no case was any obvious catalytic activity observed, and it is apparent that the proton acidity of each system is a principal factor in the conversions to **19a**, **23a**, and **24a**. Of note is that

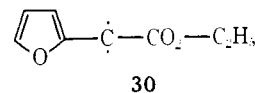
**Table III.** Photolysis of Ethyl (2-Furyl)diazoacetate (**4**)

conditions	photo sensitizer	time, min	product distribution (%) <sup>a</sup>
			<b>6</b>
CH <sub>3</sub> OH		15	<b>6</b> (32), <b>19a</b> (16), <b>20a</b> (41), <b>24a</b> (10)
CH <sub>3</sub> OH/C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	MK <sup>c</sup>	60	<b>6</b> (32), <b>19a</b> (16), <b>20a</b> (42), <b>24a</b> (10)
(CH <sub>3</sub> ) <sub>2</sub> CHOH		15	<b>6</b> (>95), <b>19c</b> (tr), <b>20c</b> (tr)
(CH <sub>3</sub> ) <sub>2</sub> CHOH/ C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	MK <sup>c</sup>	60	<b>6</b> (>95), <b>19c</b> (tr), <b>20c</b> (tr)
(CH <sub>3</sub> ) <sub>2</sub> CHOH/ C <sub>6</sub> H <sub>6</sub> <sup>b,d</sup>	MK <sup>c</sup>	60	<b>6</b> (>95)

<sup>a</sup> The yields of products are essentially quantitative. <sup>b</sup> Solvent mixture: 70/10. <sup>c</sup> Michler's ketone. <sup>d</sup> Light was passed through Corning filter no. 5970.

powdered glass functions as an acidic reagent in decomposing **4** (Table II).

The photolytic and the photosensitized decompositions of **4** in methanol and in 2-propanol were then studied to evaluate possible differences in singlet and triplet carbene processes for these systems. Irradiation of **4** in methanol with a Hanovia medium-pressure lamp (450-W) results in rapid evolution (<15 min) of nitrogen and a product mixture (Table III) of **6** (32%), **19a** (16%), **20a** (41%), and **24a** (10%). Of prime interest is that photosensitized decomposition<sup>21</sup> of **4** with Michler's ketone in methanol/benzene gives a mixture of **6**, **19a**, **20a**, and **24a** (Table III) of the same composition as from photolysis of **4** and further these product compositions are identical with that from thermolytic decomposition of **4** in methanol at 25 °C (Table I). Photolysis, photosensitization by Michler's ketone, and thermolysis of **4** in 2-propanol also give identical product mixtures: **6** (>95%) along with traces of **19c** and **20c**. It is strongly suggestive that singlet carbene or triplet carboethoxy(2-furyl)methylene (**30**), is a central



intermediate in these decomposition systems which is then partitioned by competitive carbene and cationic processes.<sup>22</sup>

## Experimental Section

Melting points were determined with a Thomas-Hoover Meltemp and are uncorrected. IR spectra were recorded on a Perkin-Elmer Infracord and NMR spectra were obtained on Varian A-60A or Jeolco MH 100 machines. Gas chromatography was effected with an Aerograph A-90P instrument. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. In several cases where slight decomposition of samples prevented acceptable analyses, exact mass measurements using an MS-9 mass spectrometer were substituted for analyses.

**Ethyl (2-Furyl)glyoxylate 2,4,6-Trimethylbenzenesulfonylhydrazide.** A mixture of ethyl (2-furyl)glyoxylate (5.04 g, 0.03 mol) and 2,4,6-trimethylbenzenesulfonylhydrazide (6.10 g, 0.029 mol) in absolute ethanol (25 mL) was refluxed for 60 min and cooled at -25 °C to give ethyl (2-furyl)glyoxylate 2,4,6-trimethylbenzenesulfonylhydrazide as yellow crystals (6.4 g, 0.017 mol, 60%); mp 106-110 °C; IR (KBr)  $\mu$  3.17 (N-H), 5.95 (-CO<sub>2</sub>R), 8.60-8.80 (-SO<sub>2</sub>-N-); NMR (CHCl<sub>3</sub>)  $\delta$  1.35 (t, 3 H, H<sub>1</sub>), 2.24 (s, 3 H, para aromatic CH<sub>3</sub>), 2.70 (s, 6 H, ortho aromatic CH<sub>3</sub>), 4.33 (q, 2 H, H<sub>2</sub>), 6.31 (m, 1 H, H<sub>3</sub>), 6.73 (m, 1 H, H<sub>4</sub>), 6.90 (s, 2 H, meta aromatic H), 7.35 (m, 1 H, H<sub>5</sub>).

Anal. Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>S: C, 56.06; H, 5.49; N, 7.70. Found: C, 56.17; H, 5.40; N, 7.61.

**Ethyl (2-Furyl)diazoacetate (4).** Tetramethylguanidine (1.15 g, 10 mmol) was added to ethyl (2-furyl)glyoxylate 2,4,6-trimethylben-

zenesulfonylhydrazone (3.64 g, 10 mmol) in methylene chloride (60 mL) at 0 °C. The mixture was stored at 0 °C for 1 h, then at -25 °C for 15 h, and the methylene chloride was removed by evaporation. The residue was triturated with ether at 0 °C. The triturate was treated with Florisil (10 g), filtered, treated with carbon dioxide (~1 g) and Florisil (10 g), and filtered. The ether was evaporated and the residual solvent removed in vacuo at 0 °C. The resulting ethyl (2-furyl)diazoacetate (**4**), a red-orange solid, mp ~25 °C, decomposes with evolution of nitrogen and exhibits strong IR absorptions at 4.80 (>C=N<sub>2</sub>) and 5.90 (-CO<sub>2</sub>R)  $\mu$ . The NMR spectrum of **4** is consistent with that expected: NMR (CCl<sub>4</sub>)  $\delta$  1.35 (t, 3 H, CH<sub>3</sub>), 4.32 (q, 2 H, CH<sub>2</sub>), 6.52 (m, 2 H, H<sub>3</sub> and H<sub>4</sub>), and 7.38 (m, 1 H, H<sub>5</sub>). The diazo ester could not be analyzed because it decomposes rapidly at room temperature.

**Thermolysis of 4.** Diazo ester **4** (0.37 g, 2.05 mmol) was volatilized at 0.3 mmHg through a Pyrex tube (6 in.) at 280 °C. The pyrolysate was collected at -78 °C. The yellow liquid product slowly decomposes at room temperature and was identified as ethyl 5-formyl-*cis*-4-penten-2-ynoate (**6**) by its IR absorption (neat) [ $\mu$  4.60 (-C=C-), 5.90-6.05 (>C=O, broad), and 6.30 (C=C)] and its NMR spectrum (CCl<sub>4</sub>) [ $\delta$  1.35 (t, 3 H, H<sub>1</sub>), 4.25 (q, 2 H, H<sub>2</sub>), 6.45 (d of d, 1 H, H<sub>4</sub>,  $J_{3,4} = 11$ ,  $J_{4,5} = 7$  Hz), 6.60 (d, 1 H, H<sub>3</sub>,  $J_{3,4} = 11$  Hz), and 10.08 (d, 1 H, H<sub>5</sub>)]. The *cis* configuration of **4** was assigned on the basis of the vinyl coupling constant of 11 Hz and the absence of IR absorption for a trans olefin.

Treatment of the pyrolysate with 2,4-dinitrophenylhydrazine reagent gave ethyl 5-formyl-*cis*-4-penten-2-ynoate 2,4-dinitrophenylhydrazone, a red solid: mp 138-139 °C dec, IR absorption (KBr)  $\mu$  4.55 (C=C), 5.87 (-CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>), 6.20 (C=N-), and 6.30 (>C=C<). The derivative exhibits NMR absorptions (CHCl<sub>3</sub>) of  $\delta$  1.35 (t, 3 H, H<sub>1</sub>), 4.30 (q, 2 H, H<sub>2</sub>), 6.12 (d, 1 H, H<sub>3</sub>,  $J_{3,4} = 11$  Hz), 7.03 (d, 1 H, H<sub>4</sub>,  $J_{3,4} = 11$  Hz), 7.95-8.50 (m, 4 H, H<sub>6</sub> and aromatic H), and 9.20 (d, 1 H, H<sub>5</sub>,  $J_{4,5} = 2$  Hz), and a mass spectral parent ion at *m/e* 332 consistent with its assigned structure.

Anal. Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>O<sub>6</sub>: C, 50.70; H, 3.60; N, 16.80. Found: C, 50.70; H, 3.72; N, 16.64.

Ynoate **6** is formed in 100% yield when aldo ester **4** in methylene chloride is kept at room temperature overnight. This procedure allows synthesis of **6** uncontaminated by small amounts of **4** remaining upon use of the pyrolytic short contact time method. Removal of the methylene chloride in vacuo gives pure **6** that can be used as starting material in subsequent experiments.

**Decomposition of 4 in Acetic Acid.** Diazo ester **4** (0.17 g, 0.95 mmol) in glacial acetic acid (5 mL) was stirred at 25 °C for 1 h. The mixture was frozen and the acetic acid sublimed in vacuo. The crude product mixture (100%) was diluted with ether, extracted with 5% sodium bicarbonate and then water, and concentrated. Upon addition of pentane, a yellow solid separated that was filtered and sublimed at 60 °C and 0.3 mmHg to yield (*Z*)- $\Delta^{3,4}$ -5-acetoxy-2-carboethoxymethylidene-2,5-dihydrofuran (**9**), a white solid: mp 98-99 °C; NMR (CCl<sub>4</sub>)  $\delta$  7.21 (broadened s, 1 H, H<sub>6</sub>), 6.52 (d, 1 H, H<sub>5</sub>,  $J_{4,5} = 7$  Hz), 6.44 (d, 1 H, H<sub>4</sub>,  $J_{4,5} = 7$  Hz), 5.10 (s, 1 H, H<sub>3</sub>), 4.19 (q, 2 H, H<sub>2</sub>), 2.12 (s, 3 H, acetoxy CH<sub>3</sub>), 1.27 (t, 3 H, H<sub>1</sub>); IR (KBr)  $\mu$  5.71 (acetate >C=O), 5.86 and 6.05 (-CO<sub>2</sub>R), 6.33 (C=C); UV (95% ethanol)  $\lambda_{\max}$  272 nm ( $\epsilon$  16 200); mass spectrum *m/e* 212 (6%, parent), 170 (66%, P - CH<sub>2</sub>=C=O), 97 (100%).

Anal. Calcd for C<sub>10</sub>H<sub>12</sub>O<sub>5</sub>: C, 56.55; H, 5.65. Found: C, 56.80; H, 5.48.

The filtrate from which **9** was isolated gave ethyl  $\alpha$ -acetoxy- $\alpha$ -(2-furyl)acetate (**10**) as a yellow oil on evaporation: NMR (CCl<sub>4</sub>)  $\delta$  7.41 (s, 1 H, H<sub>6</sub>), 6.40 (m, 2 H, H<sub>4</sub> and H<sub>5</sub>), 6.04 (s, 1 H, H<sub>3</sub>), 4.24 (q, 2 H, H<sub>2</sub>), 6.16 (s, 3 H, acetoxy CH<sub>3</sub>), 1.28 (t, 3 H, H<sub>1</sub>); IR (neat) 5.72  $\mu$  (broad, CO<sub>2</sub>R); UV (95% ethanol)  $\lambda_{\max}$  218 nm ( $\epsilon$  6300); mass spectrum *m/e* 212 (5%, parent), 170 (21%, P - CH<sub>2</sub>=C=O), 139 (12%, P - CO<sub>2</sub>Et), 97 (100%). Decomposition of **10** during chromatography prevented satisfactory elemental analysis. NMR analysis of the crude product gave the yields of **9** and **10** listed in Table I. Decomposition of **4** in ether/acetic acid (5:1) and dichloromethane/acetic acid (5:1) also yields **6**, **9**, and **10** (Table I) as determined by NMR spectroscopy.

**Decomposition of 4 in Methanol.** Diazo ester **4** (105.3 mg, 0.59 mmol) in methanol (5 mL) was stored overnight at room temperature. The red solution evolved nitrogen and turned pale yellow. Removal of the methanol gave a yellow oil (95%) that contained four products.

Formyl ester **6** (34%) was identified in the crude product mixture

by its aldehydic and vinylic NMR absorptions. The ester decomposes to nonvolatile materials upon gas chromatography.

(*E*)- $\Delta^{3,4}$ -2-Carboethoxymethylidene-5-methoxy-2,5-dihydrofuran (**24a**, 21%) could not be isolated in the crude product but was identified by its characteristic singlet NMR absorptions at  $\delta$  5.96 and 4.78. Dihydrofuran **24a** was prepared in a later experiment by cyclization of **6** in methanol (vide infra): NMR (CCl<sub>4</sub>)  $\delta$  6.20 (s, 2 H, H<sub>4</sub> and H<sub>5</sub>), 5.96 (s, 1 H, H<sub>6</sub>), 4.78 (s, 1 H, H<sub>3</sub>), 4.04 (q, 2 H, ethoxy CH<sub>2</sub>), 3.44 (s, 3 H, methoxyl CH<sub>3</sub>), and 1.30 (t, 3 H, ethoxy CH<sub>3</sub>); IR (neat)  $\mu$  5.95 and 6.07 (-CO<sub>2</sub>R) and 6.30 (C=C); UV (95% ethanol) 280 nm ( $\epsilon_{\max}$  9200); exact mass 184.073 74 (calcd for C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>, 184.073 55).

Gas chromatography of the crude product mixture on a 15% SE-30 column on Chromosorb P (6 ft) at 160 °C with helium flow of 60 mL/min allowed separation of two compounds. The first compound, a clear liquid, is ethyl  $\alpha$ -(2-furyl)- $\alpha$ -methoxyacetate (**19a**, 15%). NMR absorptions at  $\delta$  6.39 (broad s, 2 H, H<sub>4</sub> and H<sub>5</sub>) and 7.48 (broad s, 1 H, H<sub>6</sub>) indicate that **19a** is a 2-substituted furan; the remaining NMR absorptions at  $\delta$  4.85 (s, 1 H, H<sub>3</sub>), 4.25 (q, 2 H, CH<sub>2</sub>), 3.43 (s, 3 H, methoxy CH<sub>3</sub>), and 1.30 (t, 3 H, CH<sub>3</sub>) are also consistent with the assigned structure. The IR spectrum of **19a** reveals a strong absorption at 5.75  $\mu$  (unconjugated -CO<sub>2</sub>-R); the UV absorption at  $\lambda_{\max}$  220 nm ( $\epsilon_{\max}$  6300) is characteristic of furans, and the mass spectrum exhibits ions at *m/e* 184 (23%) and 111 (100%, P - CO<sub>2</sub>Et). Elemental analysis of **19a** was precluded because it decomposes in part during collection upon gas chromatography; the exact mass of **19a** is satisfactory, 184.073 77 (calcd for C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>, 184.073 55).

The second volatile product, (*Z*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-methoxy-2,5-dihydrofuran (**20a**, 27.5%), resulting from 1,5 capture of methanol, was identified by its NMR properties: NMR (CCl<sub>4</sub>)  $\delta$  7.35 (broadened d, 1 H, H<sub>5</sub>,  $J_{4,5} = 6$  Hz), 6.26 (d of d, 1 H, H<sub>4</sub>,  $J_{4,5} = 6$ ,  $J_{3,4} = 1$  Hz), 5.76 (s, 1 H, H<sub>6</sub>), 5.20 (broadened s, 1 H, H<sub>3</sub>), 4.12 (q, 2 H, CH<sub>2</sub>), 3.39 (s, 3 H, methoxyl CH<sub>3</sub>), and 1.30 (t, 3 H, -CH<sub>3</sub>). H<sub>5</sub> and H<sub>6</sub> are nearly perpendicular and thus their NMR absorptions are only slightly broadened; allylic coupling between H<sub>3</sub> and H<sub>4</sub> is small (1 Hz) as expected. Further spectral characteristics of **20a** follow: IR (neat)  $\mu$  5.95 ( $\alpha,\beta$ -unsaturated -CO<sub>2</sub>R), 6.12 and 6.35 (C=C); UV (95% ethanol)  $\lambda_{\max}$  226 nm ( $\epsilon$  6500), and 278 (12 000), calculated for **20a**  $\lambda_{\max}$  270 nm; mass spectral ions at *m/e* 184 (45%, parent ion), 153 (P - OCH<sub>3</sub>), 139 (P - OCH<sub>2</sub>CH<sub>3</sub>), and 111 (100%, P - CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); and a satisfactory exact mass, 184.073 77 (calcd for C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>, 189.073 55). Elemental analysis of **20a** was precluded because it decomposes slightly upon chromatography.

**Decomposition of 4 in Acidic Methanol.** Diazo ester **4** (56.7 mg, 0.31 mmol) was dissolved in methanol (4 mL) containing *p*-toluenesulfonic acid (25 mg, 0.15 mmol). Gas evolution proceeded readily for 30 min. The mixture was diluted with ether and extracted with 5% sodium bicarbonate and with water. Evaporation of the ether gave **6**, **19a**, **20a**, and **24a** of composition in Table I as determined by NMR spectroscopy.

**Deuterium Labeling of 19a and 20a.** Diazo ester **4** was decomposed in methanol-*O-d* (4 mL) for 2 h. The solvent was evaporated and monodeuterated **19a** and **20a** were isolated by gas chromatography. The NMR spectrum of **19a** prepared lacked the singlet H<sub>3</sub> absorption at  $\delta$  4.85 but is identical in all other respects with that of undeuterated **19a**. Compound **20a** thus obtained does not show a singlet absorption at  $\delta$  5.20 but, other than that, is identical with undeuterated **20a**.

**Deuterium Labeling of 24a.** Ester **6**, prepared by decomposition of **4** in dichloromethane at room temperature, was dissolved in methanol-*O-d* and treated with silver nitrate (10 mg). The mixture was diluted with ether, extracted with 15% ammonium hydroxide and water, and evaporated. Monodeuterated **24a** thus obtained lacks a singlet absorption at  $\delta$  4.78 but is identical in all other respects with undeuterated **24a**. Pyrolysis of monodeuterated **24a** by gas chromatography gave **20a** that is undeuterated. Thus loss of deuterium accompanies pyrolysis of **24a** to **20a**.

**Decomposition of 4 in Ethanol.** A mixture of **4** (100 mg, 0.56 mmol) in ethanol (5 mL) was stirred overnight at 25 °C. Evaporation of the solvent and NMR analysis gave **6** (64%), ethyl  $\alpha$ -ethoxy- $\alpha$ -(2-furyl)-acetate (**19b**, 12%), and (*Z*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-ethoxydihydrofuran (**20b**, 29%). Ethoxyacetate **19b**, as isolated by gas chromatography, has the following properties: NMR (CCl<sub>4</sub>)  $\delta$  7.34 (m, 1 H, H<sub>6</sub>), 6.32 (m, 2 H, H<sub>4</sub> and H<sub>5</sub>), 4.90 (s, 1 H, H<sub>3</sub>), 4.22 (q, 2 H, ester ethoxyl CH<sub>2</sub>), 3.56 (q, 2 H, ether ethoxyl CH<sub>2</sub>), and 1.30 (t, 6 H, ester ethoxyl CH<sub>3</sub> and ether ethoxyl CH<sub>3</sub>); IR (neat)  $\mu$  5.76

( $-\text{CO}_2\text{R}$ ); mass spectrum  $m/e$  198 (15%, parent), 125 (27%,  $\text{P} - \text{CO}_2\text{Et}$ ), and 97 (100%); exact mass, 198.089 37 (calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_4$ , 198.089 20).

Dihydrofuran **20b** was isolated by preparative gas chromatography: NMR ( $\text{CCl}_4$ )  $\delta$  7.47 (d, 1 H,  $\text{H}_5$ ,  $J_{4,5} = 6$  Hz), 6.46 (d, 1 H,  $\text{H}_4$ ,  $J_{4,5} = 6$  Hz), 6.05 (s, 1 H,  $\text{H}_6$ ), 5.37 (s, 1 H,  $\text{H}_3$ ), 4.16 (q, 2 H, ester ethoxyl  $\text{CH}_2$ ), 3.72 (q, 2 H, ether ethoxyl  $-\text{CH}_2-$ ), 1.25 (t, 6 H, ester ethoxyl  $\text{CH}_3$  and ether ethoxyl  $\text{CH}_3$ ); IR (neat)  $\mu$  5.95 and 6.10 ( $-\text{CO}_2\text{R}$ ), and 6.33 ( $\text{C}=\text{C}$ ); UV  $\lambda_{\text{max}}$  278 nm ( $\epsilon$  8600); mass spectrum  $m/e$  198 (23%, parent), 153 (70%,  $\text{OCH}_2\text{CH}_3$ ), and 97 (100%); exact mass, 198.089 37 (calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_4$ , 198.089 20).

**Decomposition of 4 in Acidic Ethanol.** A mixture of **4** (97 mg, 0.53 mmol) and trifluoroacetic acid (5 drops) in ethanol (10 mL) was stirred for 4 h at 25 °C. The ethanol and trifluoroacetic acid were evaporated. In addition to **6**, **19b**, and **20b** (Table I), the mixture had NMR absorption at  $\delta$  5.0 and 5.7 for (*E*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-ethoxydihydrofuran (**24b**, 15%).

**Decomposition of 4 in 2-Propanol.** A solution of **4** (101 mg, 0.56 mmol) in 2-propanol (10 mL) was stirred at room temperature for 5 h. Removal of solvent in vacuo gave **6** (>95%) containing only traces of **19c** and **20c** (Table I) as determined by NMR methods.

**Decomposition of 4 in Acidic 2-Propanol.** A mixture of **4** (103 mg, 0.57 mmol) and *p*-toluenesulfonic acid (60 mg, 0.35 mmol) in 2-propanol (10 mL) was stirred at 25 °C for 2 h. The solution was evaporated, diluted with ether, extracted with 5% sodium bicarbonate and water, and evaporated to give ethyl  $\alpha$ -(2-furyl)- $\alpha$ -(2-propoxy)-acetate (**19c**, 7%), (*Z*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-(2-propoxy)-2,5-dihydrofuran (**20c**, 53%), and (*E*)- $\Delta^{3,4}$ -2-carboethoxymethylidene-5-(2-propoxy)-2,5-dihydrofuran (**24c**, 40%) as determined by NMR spectroscopy.

Dihydrofuran **24c** could not be isolated from the mixture but characteristic NMR absorptions at  $\delta$  4.80 and 6.12 indicated its presence. Pure **24c** was prepared by cyclization of **6** in methanol (vide infra): NMR ( $\text{CCl}_4$ )  $\delta$  6.24 (br s, 2 H,  $\text{H}_4$  and  $\text{H}_5$ ), 6.12 (s, 1 H,  $\text{H}_6$ ), 4.80 (s, 1 H,  $\text{H}_3$ ), 4.05 (overlapping q and h, 3 H, ethoxyl  $\text{CH}_2$  and isopropyl CH), 1.25 (m, 9 H, ethoxyl  $\text{CH}_3$  and isopropoxyl  $\text{CH}_3$ ); IR (neat)  $\mu$  5.90 and 6.10 ( $\text{CO}_2\text{R}$ ) and 6.30 ( $\text{C}=\text{C}$ ); mass spectrum  $m/e$  212 (12%, parent), 170 (31%), 153 (31%), and 97 (100%); exact mass, 212.105 13 (calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , 212.104 85).

Dihydrofuran **20c** was isolated by gas chromatography and has the following properties: NMR ( $\text{CCl}_4$ )  $\delta$  7.38 (s, 1 H,  $\text{H}_6$ ), 6.34 (broadened s, 2 H,  $\text{H}_4$  and  $\text{H}_5$ ), 4.84 (s, 1 H,  $\text{H}_3$ ), 4.24 (overlapping q and septet, 3 H, ethoxyl  $\text{CH}_2$  and isopropyl CH), 1.30 (overlapping d and t, 9 H, ethoxyl  $\text{CH}_3$  and isopropoxyl  $\text{CH}_3$ ); IR (neat)  $\mu$  5.75 ( $\text{CO}_2\text{R}$ ); UV (95% ethanol)  $\lambda_{\text{max}}$  220 nm; mass spectrum  $m/e$  212 (15%, parent), 170 (33%,  $\text{P} - \text{OCH}(\text{CH}_3)_2$ ), 97 (100%); exact mass, 212.105 13 (calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , 212.104 85).

Furylacetate **19c** was also obtained by gas chromatography and has the following properties: NMR ( $\text{CCl}_4$ )  $\delta$  7.50 (d, 1 H,  $\text{H}_5$ ,  $J_{4,5} = 6$  Hz), 6.42 (br d, 1 H,  $J_{4,5} = 6$  Hz), 6.08 (br s, 1 H,  $\text{H}_6$ ), 5.35 (s, 1 H,  $\text{H}_3$ ), 4.18 (q, 2 H, ester  $\text{CH}_2$ ), 4.08 (heptet, 1 H, isopropoxy C-H), 1.25 (overlapping d and t, ester  $\text{CH}_3$  and isopropoxyl  $\text{CH}_3$ ); IR (neat)  $\mu$  5.90 and 6.11 ( $\text{CO}_2\text{R}$ ); UV (95% ethanol)  $\lambda_{\text{max}}$  270 nm ( $\epsilon$  11 700); mass spectrum  $m/e$  212 (12%, parent), 170 (31%,  $\text{P} - \text{CH}_2=\text{CHCH}_3$ ), 153 (31%,  $\text{P} - \text{OCH}(\text{CH}_3)_2$ ), and 97 (100%); exact mass, 212.105 13 (calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , 212.104 85).

**Silver Ion Catalyzed Decomposition of 4 in Methanol.** Silver nitrate (10 mg) was added to **4** (46 mg, 0.25 mmol) in methanol (4 mL) and vigorous evolution of nitrogen followed. The resulting pale green solution was diluted with ether, extracted with 15% ammonium hydroxide and then water, and evaporated. The yellow oil (91% yield) consisted of **19a** (11.1%), **20a** (25%), and **24a** (65%) (Table II).

**Silver Ion Catalyzed Decomposition of 4 in 2-Propanol.** Silver nitrate (10 mg) was added to **4** (70 mg, 0.39 mmol) in 2-propanol (2 mL). Nitrogen was immediately evolved. The pale green solution was diluted with ether, extracted with 15% ammonium hydroxide and water, and evaporated to give a yellow oil (85%) composed of **19c** (trace), **20c** (22%), and **24c** (78%) as determined by NMR analysis (Table II).

**Copper Ion Catalyzed Decomposition of 4 in Methanol.** Various copper reagents (Table II) catalyze decomposition of **4**. In all cases copper reagents led to complete nitrogen evolution within 1 min. Cupric acetate gave the cleanest product. In a typical experiment, cupric acetate monohydrate (10 mg) was added to **4** (71 mg, 0.39 mmol) in methanol (4 mL). The mixture turned brown (5 s) and then vigorous nitrogen evolution commenced. The resulting light yellow

solution was diluted with ether and extracted with water. Evaporation gave a yellow oil (71%) that contained **19a** (>95%) and **20a** (trace) (Table II).

**Chloroauric Acid Catalyzed Decomposition of 4 in Methanol.** Chloroauric acid (10 mg) was added to **4** (87 mg, 0.49 mmol) in methanol (4 mL) and slow, steady gas evolution ensued. After 30 min the mixture was diluted with ether, extracted with water, and evaporated to give a yellow oil (69%) containing **19a** (10%), **20a** (55%), and **24a** (35%) (Table II).

**Dichlorotetracarboxydirhodium Catalyzed Decomposition of 4 in Methanol.** Dichlorotetracarboxydirhodium (10 mg) was added to **4** (146 mg, 0.82 mmol) in methanol (4 mL). After 10 min, during which nitrogen was steadily evolved, the mixture was diluted with ether, extracted with 5% ammonium hydroxide and with water, and evaporated to give **19a** (39%), **20a** (37%), and **20a** (24%) (Table II).

**Proton-Catalyzed Isomerization of 6 to 24a.** Formyl ester **6** (65 mg, 0.43 mmol) in methanol (5 mL) was stored at room temperature for 12 h. Evaporation of the methanol gave a yellow oil composed of **6** (65%) and **24a** (35%); neither **19a** nor **20a** was found in the product by NMR spectroscopy.

**Isomerization of 6 to 24a by Silver Ion.** Silver nitrate (10 mg) was added to **6** (60 mg, 0.42 mmol) in methanol (4 mL). After 5 min the mixture was diluted with ether, extracted with 15% ammonium hydroxide and water, and evaporated to give **24a** (100%) in >97% purity. No trace of **19a** or **10a** was observed.

This method allows preparation of pure **24a-c**. When **6** reacts with silver nitrate in methylene chloride with no alcohol present, decomposition to unidentified tarry products occurs.

**Photoisomerization of 24a to 20a.** *E* isomer **24a**, prepared by silver ion catalyzed cyclization, was dissolved in dichloromethane and irradiated for 1 h with a 450-W Hanovia medium-pressure lamp. Removal of the solvent gave a mixture of **24a** and **20a** (79:21) as determined by NMR spectroscopy.

**Photolysis of 4.** A solution of **4** (150 mg, 0.84 mmol) in methanol (80 mL) was placed in a Pyrex test tube parallel to an immersion well and irradiated with a 450-W Hanovia medium-pressure lamp. Nitrogen evolution was complete within 15 min. The solvent was removed and the residue was analyzed by NMR spectroscopy. The product distribution is given in Table III. A similar experiment was performed using 2-propanol as solvent (Table III). The product mixtures from photolysis and thermolysis of **4** in methanol are identical. Photolysis and thermolysis of **4** in 2-propanol also give products of identical composition.

**Sensitized Photolysis of 4.** Diazo ester **4** (150 mg, 0.84 mmol) and Michler's ketone (0.59 g, 2.2 mmol) were dissolved in a mixture of 2-propanol/benzene (70:10) and placed in a Pyrex tube. The lower one-fourth of the tube was immersed in an ice bath and the temperature of the stirred solution was kept at  $\sim 10$  °C throughout photolysis. Under these conditions thermolysis of **4** is noncompetitive. Light from a 450-W Hanovia medium-pressure lamp was filtered by a Corning no. 3718 uranium glass filter ( $\lambda$  330 nm). This filter assures that the sensitizer absorbed >98% of light entering the solution. After 1 h, nitrogen evolution ceased. The solvent was removed in vacuo and ether (50 mL) was added to the residue. The ether solution was filtered to remove undissolved Michler's ketone, extracted with 10% hydrochloric acid and water, dried, and evaporated to give a yellow oil that was analyzed by NMR. The only product observed was **6** (Table III).

In similar experiments, the sensitized photolyses of **4** were carried out in methanol/benzene (80:10), cumene/benzene (70:10), and methanol/benzene (70:10). The product distributions as determined by NMR spectroscopy are given in Table III. To assure that long-wavelength absorption by **4** was not causing its direct photolysis, the sensitized photolysis of **4** in 2-propanol/benzene (70:10) was repeated using a Corning No. 5970 filter which has transmission characteristics  $310 < \lambda < 400$ . This filter brackets the maximum absorption of Michler's ketone (366 nm) and assures primary excitation of only the photosensitizer. No difference in either the time of photolysis or the products was observed (Table III).

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## References and Notes

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- (8) The rate of decomposition of **4** is not greatly affected by addition of acetic acid, benzoic acid in ethyl ether, or various alcohols. Acid-catalyzed decomposition does not appear to be a major response of **4** under these conditions.
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- (16) (a) Diphenyldiazomethanes decompose in alcoholic and in aqueous solvents via diphenylcarbene intermediates to yield benzhydryl alkyl ethers and benzhydrols. These processes do not involve nucleophilic attack of the diazo compounds on the hydroxylic solvents to form diazonium or carbenium ion intermediates. Phenyl diazomethanes, however, are decomposed by hydroxylic solvents via diazonium ion mechanisms. (b) D. Bethell, D. Whittaker, and J. B. Callister, *J. Chem. Soc.*, 2466 (1965). (c) D. Bethell and R. D. Howard, *J. Chem. Soc. B*, 745 (1969). (d) D. Bethell, A. R. Newall, and D. Whittaker, *ibid.*, 23 (1971). (e) R. J. Miller, Ph.D. Dissertation, The Ohio State University, 1975. (f) D. Bethell and D. Whittaker, *J. Chem. Soc. B*, 778 (1966).
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- (21) The UV spectrum of **4** has  $\lambda_{\text{max}}$  220 nm ( $\epsilon$  5000), 240 (5900), and 300 (4100). The long wavelength trails into the red region and at 366 nm has an extinction coefficient of <200. Use of a 2 M excess of Michler's ketone assures that the photosensitizer absorbs >98% of the incident light at 366 nm. The light was filtered (Corning no. 3718,  $\lambda > 330$  nm) to prevent primary excitation of **4** at lower wavelengths.
- (22) (a) The intra- and the intermolecular products of photolysis and photosensitization of (2-*n*-butylphenyl)diazomethane in cyclohexane are identical.<sup>22b</sup> Similarly, there is no difference in the respective intramolecular products of photolytic and photosensitized decompositions of methyl  $\alpha$ -diazo-2,3-dimethylcyclopropane ( $1\alpha, 2\alpha, 3\beta$ )acetate,<sup>22c</sup> methyl  $\alpha$ -diazo-2,3-dimethylcyclopropane ( $1\alpha, 2\beta, 3\beta$ )acetate,<sup>22c</sup> and ethyl  $\alpha$ -diazophenylthiolacetate.<sup>22d</sup> On the other hand, the respective carbenic products of photolysis and photosensitization of 2-methyl-2-phenyldiazopropane,<sup>22e</sup> the sodium salt of brexan-4-one tosylhydrazone,<sup>22f</sup> and alcoholic solutions of diazoacetophenone<sup>22g</sup> vary greatly. (b) T. A. Baer and C. D. Gutsche, *J. Am. Chem. Soc.*, **93**, 5180 (1971). (c) R. R. Gallucci and M. Jones, Jr., *ibid.*, **98**, 7704 (1976). (d) G. G. Orphanides, Ph.D. Dissertation, The Ohio State University, 1972. (e) J. J. Havel, *J. Org. Chem.*, **41**, 1464 (1976). (f) A. Nickon, F. Huang, R. Weglein, K. Matsuo, and H. Yagi, *J. Am. Chem. Soc.*, **96**, 5264 (1974). (g) A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965).

## Photolysis of *tert*-Butyl Hydroperoxide in Alcohols. A Carbon-13 CIDNP Study<sup>1</sup>

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**Abstract:** We have observed carbon-13 CIDNP during photolysis of *tert*-butyl hydroperoxide (*t*-BuOOH) in a variety of alcohols. Interpretation of this CIDNP provides mechanistic insight into the photodecomposition. Most notable was the detection of simple enols **5** and *tert*-butylperoxy compounds **3** as transient intermediates. A major polarization pathway was the free-radical encounter of *tert*-butylperoxy and ketyl radicals. Production of  $\beta$ -hydroxy radicals was a preferential polarization route for 2-methylpropanol (**1E**) and 3-methyl-2-butanol (**1L**).

### Introduction

Our interest in the mechanism of hydrocarbon autoxidation led us to use carbon-13 CIDNP to study the photochemical decomposition of *tert*-butyl hydroperoxide in a variety of alcohols. We anticipated obtaining intimate mechanistic details about the autoxidation process through understanding more fully the radical chemistry of hydroperoxides. Carbon-13 CIDNP has been a powerful tool for elucidating the elementary processes of radical decompositions.<sup>5</sup> Hydroperoxides and alcohols are formed during the autoxidation process.<sup>6</sup> Although their thermal reactions have been characterized, the photo-

chemical reactions of hydroperoxides have not been extensively studied.<sup>6,7</sup> Photochemical initiation of hydroperoxide decomposition allows independent control of reaction conditions, a distinct advantage for carbon-13 CIDNP using Fourier transform NMR.<sup>8-10</sup>

### Experimental Section

**NMR Measurements.** The spectrometer system was a modified Varian HA-100 operating at 25.15 MHz with an external fluorine-19 field-frequency lock. A NIC-80 data system was used for signal accumulating and processing. A 90° pulse took 105  $\mu$ s. The spectral