# CONCLUSIONS

1. The chain-transfer constants in the telomerization of ethylene and propylene by methyl isobutyrate  $(C_n)$  vary relatively slightly with extension of the radical chain length, indicating polar effects in the chain-transfer step in these systems.

2. Nonmonotonic change in  $C_n$  with increasing n is found for the propylene-methyl isobutyrate system with a minimum at n = 3, which is attributed to rearrangement of the radicals with three monomer units with a 1,5-hydrogen migration from the tertiary carbon atom in the  $\gamma$  position relative to the carbomethoxyl group.

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# HOMOLYTIC OXOALKYLATION OF FURAN, $\alpha$ -METHYLFURAN, AND THIOPHENE

# R. S. Min, V. S. Aksenov, M. G. Vinogradov, and G. I. Nikishin

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Homolytic substitution in the ring of heteroaromatic compounds has not been subjected to extensive study, and most studies in this area are devoted to the reaction of heterocyclic compounds with aryl radicals [1]. There have been only a few studies on the reactions of thiophene and furan compounds with alkyl radicals [2-4].

This work is devoted to a study of homolytic substitution reactions in the ring of furan,  $\alpha$ -methylfuran, and thiophene by the CH<sub>2</sub>COCH<sub>3</sub> radical generated in the acetone -Mn(OAc)<sub>3</sub> -AcOH system [5] and the CH<sub>3</sub>COCHCOCH<sub>3</sub> radical generated from acetylacetone.

The homolytic oxoalkylation of furan,  $\alpha$ -methlyfuran, and thiophene\* proceeds regiospecifically at the  $\alpha$ -carbon atom of the heteroaromatic ring. As a result of the reaction of these compounds with the CH<sub>3</sub>COCH<sub>2</sub> radical, ketones (Ia-c) are obtained in 35-60% yield relative to manganese triacetate (MTA)



\*A preliminary report on the reaction of the  $CH_3 COCH_2$  radical with thiophene was given in our previous communication [5].

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Under the conditions selected, products of the acetoxylation and dehydrodimerization of ketones (I), namely, (IV) and (V), are formed, though in only 2-3% yield. The structure of 1,4-diketones (V) was demonstrated by their conversion to 3,4-bis(2-heteroaryl) derivatives of furan (VI)



Special experiments on the oxidation of ketones (I) by MTA showed that this reaction is interesting in itself since it may be controlled to give selective formation of acetoxyketones (IV) and 1,4-diketones (V) by varying the oxidation conditions.

Acetoxyketones (IV) are obtained exclusively in acetic acid from ketones (I) at high MTA concentrations as a result of the oxidation of intermediate radicals (II) by Mn(III) ions, which was rather unexpected since 2-oxoalkyl radicals are electrophilic in nature and do not tend to undergo oxidation with electron transfer by metal ions [6]. For example, the formation of only the products of the recombination of intermediate radicals was noted in the reaction of benzyl ketones with MTA [6]. In this case, the formation of the carbocation intermediate (III) is facilitated by the electron-donor nature of the furan and thiophene ring\* and the stabilizing effect of the heteroaryl substituent is stronger in this case than the destabilizing effect of the carbonyl group.

This assumption is supported by the finding that the oxidation of radical (IIa, R = H) obtained in acetic acid with [MTA] = 0.2 mole/liter yields acetoxyketone (IVa) and dehydrodimer (Va) in 1:1.5 ratio, while virtually only acetoxy derivative (IVb) is obtained from (IIb) upon the introduction of the electron-donor methyl group into the furan system. The same effect causes the substitution of oxygen in the heteroaromatic ring of radical at the more nucleophilic heteroatom, sulfur [radical (IIc)].

At low MTA concentration, radical recombination leading to diketones (V) predominates regardless of the structure of the intermediate radical (II). Thus, as a result of the oxidation ketone (Ic) in AcOH for [MTA] = 0.04 mole/ liter, ketones (IVc) and (Vc) are formed in 1:4 ratio. For preparative purposes, it is convenient to carry out the oxidation ketones (I) to yield 1,4-diketones in benzene medium, in which MTA is only slightly soluble and the oxidation of intermediate radicals (II) virtually does not occur.

The PMR and <sup>13</sup>C NMR data indicate that the dimerization of radicals IIa and IIb proceeds stereoselectively with the probable formation of the  $d_i$ -diastereomer since a donor-acceptor interaction of the ring heteroatom is possible in this c ase with the carbonyl group leading to a gain in energy



If this assumption is justified, then the difference in energy between the meso and d, l configurations of diketone (IIc) should be less than in diketone (IIb) as a consequence of the reduced nucleophilicity of the thiophene ring (but not of the sulfur atom). Indeed, a mixture of meso and d, l isomers of (Vc) in 1:3 ratio was obtained upon the recombination of radicals (IIc).

The addition of the 1,3-dioxoalkyl radical (VII) generated in the acetylacetone – MTA – AcOH redox system to furan and  $\alpha$ -methylfuran also leads to products of substitution exclusively at the  $\alpha$ -carbon atom of the heteroaromatic ring. The 1,3-diketones formed are mostly in the enol form (the enol fraction is >95% according to PMR data). The dehydro dimer (IX) is present in the products of the reaction of acetylacetone with  $\alpha$ -methylfuran, in addition to tautometry of (VIIIb)

 $\begin{array}{c} MeCOCH_{2}COMe \xrightarrow{MTA} MeCOCHCOMe \\ \hline \\ (VII) \end{array}$ 

\*For example (2-furyl)carbinol in acid medium readily forms the 2-furylmethyl cation [7].

Spectral Data for Acetoxyketones (IV) and 1,4-Diketones (V)	1 <sup>3</sup> CNMR spectrum 6, ppm	13.42 (CH <sub>3</sub> ), 20.40 (CH <sub>3</sub> COO), 26.17 (CH <sub>3</sub> CO), 73.82 (CH), 107,08 & 112.80 (C <sup>3</sup> & C <sup>4</sup> ), 169,99 (CO), 199,25 (COO)			13,42 (2CH <sub>3</sub> ), 28,60 (2CH <sub>3</sub> CO), 53,18 (2CH), 106,67 & 109,70 (2C <sup>3</sup> & 2C <sup>4</sup> ), 147,53 & 152,26 (2C <sup>2</sup> & 2C <sup>3</sup> ), 204,35 (2CO)	28,78 & 29,87 (2CH <sub>3</sub> CO), 56,50 & 57,43 (2CH), 125,67 & 125,85 (2C <sup>3</sup> ), 126,95, 127,07, 127,37 & 127,74 (2C <sup>3</sup> & 2C <sup>3</sup> ), 137,39 & 137,81 (2C <sup>2</sup> ), 205,03 & 206,24 (2CO)
	PMR spectrum 6, ppm, J, Hz	$2,07_{s}$ (2CH <sub>3</sub> ), 2,29 s (CH <sub>3</sub> ), 5,92 s (CH), 5,98-6,27 m (H <sup>3</sup> & H <sup>4</sup> )	$\begin{array}{c} 2.03 & (2 \mathrm{CH}_3), 6, 45 \\ 7,06 & (\mathrm{H}^4), 7, 29 \\ J_{4-5} = 5, 2; \ J_{3-5} = 1, 2 \end{array}  (\mathrm{H}^5); \ J_{3-4} = 3, 6 \\ J_{4-5} = 5, 2; \ J_{3-5} = 1, 2 \end{array}$	$2,10 \text{ s} (2\text{CH}_3), 4,54 \text{ s} (2\text{CH}), 5,94-6,12 \text{ s} (2\text{CH}^3 \& 2\text{H}^4), 7,16-7,20 \text{ m} (2\text{H}^5)$	<b>2.07</b> s (2CH <sub>3</sub> ), 2,13 s (2CH <sub>3</sub> ), 4,47 s (2CH), 5,63-5,90 m (2H <sup>3</sup> & 2H <sup>4</sup> )	1,92s & 2,11s (2CH <sub>3</sub> ), 4,53s & 4,63s (2CH), 6,55-7,30m (2H <sup>3</sup> , 2H <sup>4</sup> & 2H <sup>5</sup> )
	UV spectrum $\lambda$ , nm( $\epsilon$ )			217 (13 600) 280 (1730)	225 (17 300) 285 (2500)	238 (15 300) 285 (1300)
	IR spectrum v, cm <sup>-1</sup>	787, 3125, (tmg), <b>1230</b> (C-O-C), 1733, 1750 (C=O)	720, 845, 3450 (ting), 1235 (C-O-C), 1740, 1752 (C=O)	760, 3135, 3150 (ring), 1720 (C=O)	786, 3125 (ring), 1720 (C=O)	705, 720, 855 (ring),
TABLE 1.	Compound	(IVb)	(IVc)	(Va)	(qA)	(Vc)

. LE 1. Spectral Data for Acetoxyketones (IV) and 1,4-Diketones



Dehydrodimer (IX) was also obtained in the direct oxidation of (VIIIb) by MTA in acetic acid. The structure of dehydrodimer (IX) was proven using PMR, <sup>13</sup>C NMR, IR, UV, and mass spectrometry. This pathway for the dehydrodimerization of ketone (VIIIb) leading to the C–O dehydro dimer may be attributed to the high degree of enolization of the starting diketone (VIIIb) and the steric hindrance in the case of C–C dehydrodimerization created by the four acetyl substituents at the neighboring quaternary carbon atoms.

## **EXPERIMENTAL**

The PMR spectra were taken on Varian DA-60-IL and Tesla BS-487 spectrometers in  $CCl_4$  with TMS as the internal standard. The <sup>13</sup>C NMR spectra were taken in the pulse mode on a Bruker WR-60 spectrometer with 15.08 MHz working frequency in  $CDCl_3$  with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer for samples in a thin layer and KBr pellets. The UV spectra were obtained on a Specord UV-VIS spectrophotometer in hexane. The mass spectra were obtained on Varian MAT CH-6 and MAT CH-III spectrometers using direct and chromatographic introduction to the ion source at 70 and 50 eV, respectively. The gas—liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with flame-ionization detector and 2 m  $\times$  3 mm column packed with 5% SE-30 and 15% PEG-40M + 0.5% terephthalic acid on Chromaton N-AW.

A sample of MTA dihydrate was obtained according to a handbook procedure [8]. The Mn(III) content, according to cerimetric analysis, was 19.1% (calculated 20.5%). Chemically pure grade acetone and acetic acid were used without further purification, and the starting heteroaromatic compounds and acetylacetone were purified by distillation.

Reaction of Acetone with Heteroaromatic Compounds. Method A [5]. A mixture of 1 mole acetone, 0.05 mole MTA, and 0.25 mole heteroaromatic compound in 50 ml acetic acid was shaken in an ampul at 70-80°C until the disappearance of the brown color of MTA. The mixture was filtered, and the excess of starting compounds was distilled off. The residue was poured into water and extracted with ether. The extract was washed with water, dried, and distilled.

Method B. A sample of 1 mole Mn(OAc), 4H, O was dissolved in 150 ml acetic acid in a round-bottom four-

necked flask equipped with a mechanical stirrer, reflux condenser, thermometer and inlet tube for argon at  $90-95^{\circ}$ C. Then, 0.025 mole KMnO<sub>4</sub> was added periodically in small batches, the reaction mixture was stirred for 0.5 h at  $90-95^{\circ}$ C, and 40 ml acetic acid was added. The reaction mixture was cooled to  $60^{\circ}$ C, and a mixture of 1 mole heteroaromatic compound and 3 moles acetone was added. The stirring was continued at  $60^{\circ}$ C in an argon stream until the solution lost its color. The reaction mixture was treated as in Method A.

The yields of compounds with the exception of (IVa-c) are given relative to MTA. The spectral data for (IVb, c) and (Va, b) are given in Table 1.

2-Acetonylfuran (Ia). Compound (Ia) was obtained from acetone and furan according to method A with a yield of 1 g (35%), bp 70-72°C (15 mm) [9]. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 745 (CH=), 1720 (C=O). PMR spectrum ( $\delta$ , ppm): 1.98 s (CH<sub>3</sub>CO), 3.55 s (CH<sub>2</sub>CO), 6.07-6.27 m (H<sup>3</sup> and H<sup>4</sup>), and 7.25 m (H<sup>5</sup>).

2-Acetonyl-5-methylfuran (Ib). Compound (Ib) was obtained by methods A and B from acetone and  $\alpha$ -methylfuran in 1.7 g yield (50%), bp 76°C (10 mm) [10]. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 790 (CH=), 1720 (C=O). PMR spectrum ( $\delta$ , ppm): 2.04 s (CH<sub>3</sub>CO), 2.18 (CH<sub>3</sub>), 3.53 s (CH<sub>2</sub>CO), 5.84-6.01 m (H<sup>3</sup> and H<sup>4</sup>).

2-Acetonylthiophene (Ic). Compound (Ic) was obtained by method B in 1.4 g yield (40%), bp 82°C (5 mm) [11]. The PMR spectrum is given in our earlier work [5].

1-Acetoxy-1-(2-furyl)propan-2-one (IVa). A mixture of 0.02 mole ketone (Ia), 0.02 mole MTA, and 50 ml acetic acid was stirred at 80°C until the brown color of MTA disappeared. The mixture was treated with water, extracted with ether, dried, and distilled. A yield of 0.2 g (10%) (IVa) was obtained, bp 98-100°C (0.2 mm). PMR spectrum ( $\delta$ , ppm):

2.05 s (2CH<sub>3</sub>), 5.75 s (CHO), 6.37-6.56 m (H<sup>3</sup> and H<sup>4</sup>), 7.56-7.58 m (H<sup>5</sup>).

1-Acetoxy-1-(5-methyl-2-furyl)propan-2-one (IVb). Compound (IVb) was obtained as indicated above from ketone (Ib) in 0.4 g (20%) yield, bp 67-68°C (0.2 mm), M<sup>+</sup> 196. Found: C 61.04; H 6.02%. Calculated for  $C_{10}H_{12}O_4$ : C 61.12; H 6.12%.

1-Acetoxy-1-(2-thienyl)propan-2-one (IVc). Compound (IVc) was obtained as indicated above from ketone (Ic) in 0.5 g (25%) yield, bp 86-88°C (0.1 mm). Found: C 54.95; H 5.19; S 16.0%. Calculated for  $C_9H_{10}O_3S$ : C 54.55; H 5.05; S 16.1%.

3,4-Di(2-furyl)hexane-2,5-dione (Va). A mixture of 0.07 mole ketone (Ia), 0.07 mole MTA, and 180 ml benzene was stirred and heated at reflux until loss of color (4-5 h). The mixtured was filtered to remove Mn(II) salts, benzene was distilled off, and the residue was distilled. A yield of 0.9 g (10%) (Va) was obtained, bp 116-118°C (0.15 mm), M<sup>+</sup> 246. Found: C 67.75; H 5.76%. Calculated for  $C_{14}H_{14}O_4$ : C 68.29; H 5.69%.

3,4-Di(5-methyl-2-furyl)hexane-2,5-dione (Vb). Compound (Vb) was obtained as indicated above from ketone (Ib) in 1.0 g (10%) yield, bp 110-112°C (0.1 mm), mp 47°C, M<sup>+</sup> 274. Found: C 69.67; H 6.67%. Calculated for  $C_{16}H_{18}O_4$ : C 70.07; H 6.57%.

3,4-Di(2-thienyl)hexane-2,5-dione (Vc). Dione (Vc) was obtained as indicated above from ketone (Ic) in 1.6 g (15%) yield (mixture of diastereomers), bp 118-120°C (0.03 mm), M<sup>+</sup> 278. The spectral data are given in Table 1. Crystals of the meso form of (Vc) were obtained from EtOH, mp 148°C. PMR spectrum ( $\delta$ , ppm): 1.92 s (2CH<sub>3</sub> CO), 4.63 s (2CHC), 6.80-7.20 m (2H<sup>3</sup>, 2H<sup>4</sup>, and 2H<sup>5</sup>).

2,5-Dimethyl-3,4-di(2-furyl)furan (VIa). A sample of 0.01 mole 1,4-diketone (Va) in 100 ml acetic acid was heated for 4-5 h at 140-150°C. The mixture was treated with water, extracted with  $CCl_4$  and the extract was dried with water, dried, and distilled. A yield of 0.45 g (20%) (VIa) was obtained with bp 110-112°C (0.15 mm), M<sup>+</sup> 228. PMR spectrum ( $\delta$ , ppm): 2.30 s (2CH<sub>3</sub>), 6.46-6.95 m (2H<sup>3</sup> and 2H<sup>4</sup>), 7.40-7.48 m (2H<sup>5</sup>).

2,5-Dimethyl-3,4-(5-methyl-2-furyl)furan (VIb). A sample of (VIb) was obtained as indicated above from 1,4diketone (Vb) in 0.75 g (30%) yield, bp 106-108°C (0.1 mm). UV spectrum ( $\lambda$ , nm ( $\epsilon$ )): 221 (8800), 275 (5000), 330 (3600). Mass spectrum, m/z (rel. int., %): 257 (13), 256 (M<sup>+</sup> 73), 230 (20), 218 (52), 214 (20), 213 (97), 180 (42), 175 (17), 165 (14), 151 (13), 150 (60), 149 (69), 145 (20), 137 (35), 129 (13), 119 (18), 115 (16), 95 (19), 81 (13), 43 (100). PMR spectrum ( $\delta$ , ppm): 2.26 s (2CH<sub>3</sub>), 2.33 s (2CH<sub>3</sub>), 5.85 s (2H<sup>3</sup> and 2H<sup>4</sup>).

2,5-Dimethyl-3,4-di(2-thienyl)furan (VIc). A sample of (VIc) was obtained as indicated above from 1,4-diketone (Vc) in 1.3 g (50%) yield, bp 115-117°C (0.03 mm). UV spectrum ( $\lambda$ , nm ( $\epsilon$ )): 214 (22,400), 240 (39,300), 330 (1300). PMR spectrum ( $\delta$ , ppm): 2.28 s (2CH<sub>3</sub>), 6.57-7.12 m (2H<sup>3</sup>, 2H<sup>4</sup>, and 2H<sup>5</sup>).

**Reaction of Acetylacetone with**  $\alpha$ -Methylfuran. A mixture of 0.13 mole acetylacetone, 0.07 mole MTA, 0.07 mole  $\alpha$ -methylfuran, and 80 ml acetic acid was shaken in an ampul at 80°C until the disappearance of the brown color of the Mn(III) salt (1 h). The reaction mixture was filtered, poured into water, and extracted in ether. The extract was washed with water and 2% aq. sodium carbonate, dried, and distilled to yield 1.0 g (14%) (VIIIb) and 1.9 g (15%) (IXb).

**3-(5-Methyl-2-furyl)pentane-2,4-dione (VIIIb)**, bp 98-100°C (10 mm). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 790, 3110 (ring), 1565-1624 (C=COH), 1680, 1710 (C=O). PMR spectrum ( $\delta$ , ppm): 1.85 s (CH<sub>3</sub>), 2.25 s (CH<sub>3</sub>), 5.70-6.05 m (H<sup>3</sup> and H<sup>4</sup>), 16.72 s (OH). Found: C 67.32, H 6.82%. Calculated for C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>: C 67.67; H 6.67%.

**6-AcetyI-4-methyI-3,6-di(5-methyI-2-furyI)-5-oxaoct-3-ene (IXb)**, bp 148-150°C (0.05 mm), mp 110°C. IR spectra ( $\nu$ , cm<sup>-1</sup>): 800, 3140 (ring), 1255 (C-O-C), 1640 (C=C), 1710, 1730 (C=O). UV spectrum ( $\lambda$ , nm( $\epsilon$ )): 218 (17,700), 281 (9800), M<sup>+</sup> 358. PMR spectrum ( $\delta$ , ppm): 1.75 s (2CH<sub>3</sub> CO), 2.10 (CH<sub>3</sub> CO), 2.20 s (CH<sub>3</sub>), 2.28 s (2CH<sub>3</sub>), 5.80-6.25 m (2H<sup>3</sup> and 2H<sup>4</sup>). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 13.11 (CH<sub>3</sub>), 13.72 (CH<sub>3</sub>), 15.10 (CH<sub>3</sub>), 23.68 (2CH<sub>3</sub> CO), 28.90 (CH<sub>3</sub> COC=), 73.29 (C-O), 107.03 and 109.10 (2C<sup>3</sup> and 2C<sup>4</sup>), 111.47 (=C-CO), 147.00 and 152.26 (2C<sup>2</sup> and 2C<sup>5</sup>), 152.87 (=C-O), 193.36 (CO), 201.86 (2CO). Found: C 67.04; H 6.30%. Calculated for C<sub>20</sub>H<sub>22</sub>O<sub>6</sub>: C 67.03; H 6.14%.

3-(2-Furyl)pentane-2,4-dione (VIIIa). Dione (VIIIa) was obtained from acetylacetone and furan as described above in 0.3 g (5%) yield, bp 47-49°C (10 mm). PMR spectrum ( $\delta$ , ppm): 1.93 s (2CH<sub>3</sub>), 6.15-6.40 m (H<sup>3</sup> and H<sup>4</sup>, 7.35-7.45 m (H<sup>5</sup>), 16.72 s (OH).

#### CONCLUSIONS

1. Homolytic substitution in the heteroaromatic ring of furan,  $\alpha$ -methylfuran, and thiophene by CH<sub>3</sub>COCH<sub>2</sub> and CH<sub>3</sub>COCHCOCH<sub>3</sub> radicals generated from acetone and acetylacetone using Mn(III) acetate (a one-electron oxidizing agent) proceeds regiospecifically at the  $\alpha$ -carbon atom of the ring and leads to 2-furyl- and 2-thienyl ketones.

2. Acetoxylation and C-C or C-O dehydrodimerization occurs in the oxidation of 2-furyl- and 2-thicnyl ketones by Mn(III) acetate. The reaction pathway depends on the concentration of  $Mn(OAc)_3$ .

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GEMINAL SYSTEMS. 15\*. CHEMICAL PROPERTIES OF N-CHLORO-N-ALKOXY-N-tert-ALKYLAMINES

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N-Halo-N-alkoxy-N-alkylamines is a class of organic compounds that remains virtually unstudied. Only some perfluoro derivatives of this class have been described [2]. N-Chloro-N-alkoxy-N-alkylamines (CAA) were unknown until recently [3]. CAA derivatives containing a proton in the  $\alpha$ -position of the N-alkyl substituent readily undergo dehydrochlorination to yield oxime O-ethers [3-5], while N-trityl and N- $\alpha$ -oxyalkyl-substituted derivatives rearranged with the migration of Ph, R, and CO<sub>2</sub> R groups to the nitrogen atom of the  $\alpha$  substituents [6]. Study of CAA became possible after synthesis of the relatively stable N-chloro-N-alkoxy-N-tert-alkylamines (CATA) [3, 5]. CATA are interesting from the viewpoint of comparison of the well-studied N-chloroamines (see reviews [7-9]). Similar to N-chloroamines, these compounds give a positive oxidative test with KI and are alkoxyaminating reagents. In this regard, they may be seen as aza analogs of  $\alpha$ -haloalkyl ethers having  $\alpha$ -alkoxyalkylating action [10]. This analogy led to the study of the reaction of CATA with alcohols in the presence of bases and the discovery of facile nucleophilic substitution at the nitrogen atom with the formation of N, N-dialkoxyamines [3, 5]. Study of the chemical properties of CATA was extended in the present work.

The facile loss of the chloride anion from CATA is apparently related to the formation of resonance-stabilized nitrenium—oxonium ions (NOI). The display of ambident properties by NOI relative to nucleophiles ( $X^{-}$ ) may be expected by analogy with carboxonium ions, for which the reaction of type A proceeds with kinetic control while the reaction of type B proceeds with thermodynamic control [10]; path A is favored for strong nucleophiles, while path B is favored for weak nucleophiles

$$R = MeO_{2}CCMe_{2} (a); MeO_{2}CCH_{2}CMe_{2} (b) \bullet$$

$$R = MeO_{2}CCMe_{2} (a); MeO_{2}CCH_{2}CMe_{2} (b) \bullet$$

$$R = MeO_{2}CCMe_{2} (b); MeO_{2}CCH_{2}CMe_{2} (b) \bullet$$

$$R = MeO_{2}CCMe_{2} (b); MeO_{2}CCH_{2}CMe_{2} (b) \bullet$$
(A)

Both these pathways are found for reactions of CATA with alcohols, but pathway A predominates and nitroso compounds are formed in only small amounts [5].

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<sup>\*</sup>For Communication 14, see ref. [1].