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PHOTOCHEMICAL AND THERMAL ADDITION OF ALCOHOLS TO 2-CYANOFURAN

1-ALKOXY-2-CYANOCYCLOPROPANE-3-CARBOXALDEHYDES; 2-ALKOXY-3-CYANO-2, 3-DIHYDROFURAN; 1-ALKOXY-1-(2-FURAN)-METHYLENIMINE; PHOTOCHEMICAL RING CONTRACTION; *CIS-TRANS*-ISOMERIZATION OF DIHYDROFURANS

H. Hiraoka*
IBM Research Laboratory, San Jose, California

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Abstract—The photolysis of 2-cyanofuran in alcohols yields 1-alkoxy-2-cyanocyclopropane-3-carboxaldehydes as the major products, which rearrange thermally to *trans*-2-alkoxy-3-cyano-2, 3-dihydrofurans and small amounts of *cis*-isomers. Thermal mutual rearrangements between *trans*- and *cis*-2-alkoxy-3-cyano-2, 3-dihydrofurans were studied. Liquid phase thermal addition of alcohols in a temperature range between 100° and 200° yields 1-alkoxy-1-(2-furan)-methylenimines, which rearrange photochemically to 2-furyl-methylamino-ketone in case of the methoxy derivative. 3-Cyano-furan does not yield photoaddition or thermal addition products. The different behaviors of 2- and 3-substituted furans are discussed.

Five-membered cyclic compounds undergo valence isomerizations under the influence of UV light in two different ways: Ring contractions to yield cyclopropenyl compounds, and bicyclizations to yield Dewar type isomers. Furans,[1] isoxazoles,[2] pyrazoles,[3] and possibly thiophenes[4] belong to the first class, and cyclopentadiene,[5] pyrazolenines,[6] and pyrroles[7] to the second class. A short communication treating differences of photochemical reactions of furan and pyrrole was reported,[7] while 2-methoxy-3-cyano-2,3-dihydrofuran was claimed to be a major photoproduct of 2-cyanofuran in methanol.[8] The present paper gives a full account of the photochemical addition of an alcohol to 2-cyanofuran, and compares it with the thermal addition.

Photoproducts and mechanism of photochemical reactions

The 254 nm irradiation of 2-cyanofuran in a methanol solution yields almost exclusively the adducts of methanol and 2-cyanofuran. The main mass spectrum peaks of the adducts are located at *m/e* 126 (8%), 125 (parent peak, 81%), 110 ($\cdot O\overline{CHCHCNC}HCHO$, 30%), 96($CH_3O\overline{CHCH\text{-}CNC}H\cdot$, base peak 100%) 94($\cdot\overline{CHCHCNC}HCHO$, 58%), 93($\overline{CH{=}CCNC}HCHO$, 36%), 82(57%), 66(61%), 55(73%), 39($\cdot\overline{CHCH{=}C}H$, 55%), 31 ($\cdot OCH_3$, 20%), 29($\cdot CHO$, 70%), 28(CO, 29%). The mass spectrum indicates the products to be aldehydes by relatively large peaks at *m/e* 96 and 29. The neat IR spectrum of the adducts also shows aldehyde absorptions at 2860, 2760(ν H-CO), 1720(ν C=O) cm^{-1} in addition to C-H stretching vibration in cyclopropane ring at 3040 cm^{-1}: other main peaks are located at 2950, 2250 (ν C≡N), 1460, 1400, 1225, 1190, 1140, 1070, 975, and 910 cm^{-1}. Moreover, addition of 2,4-dinitrophenyl-hydrazine reagent to the irradiated solutions affords yellow crystals, indicating presence of aldehyde groups. The NMR spectrum, as shown in Fig 1, indicates two different aldehyde groups at τ 0·45 (d, J = 3·5 Hz), and τ 0·72 (t, J = 3·3 Hz), together with a small amount of a third aldehyde which has an NMR absorption at τ 0·72 (d, J = 3·3 Hz) inside the triplet, as shown in an expanded scale; relative ratio 0·52:0·39:0·09. The other NMR signals are located at τ 6·0(m), 6·6 (two large and one small singlets, CH_3O), 7·5(m), and 7·8(q): relative intensities to the combined aldehyde signals are 1:3:1·5:0·5. Interestingly there is no olefinic hydrogen appearing in the NMR spectrum. Relatively large coupling constants for the aldehyde hydrogens indicate that the adducts are cyclopropane carboxaldehydes,[9] which also agree with the observed IR absorptions attributed to aldehyde groups and cyclopropane rings. On the basis of the spectroscopic evidence and of the thermal rearrangements discussed in the following section, the adducts are concluded to be a mixture of 1-cyano-*trans*-2-methoxy-cyclopropane-*trans*-3-carboxaldehyde, (**1**), and 1-cyano-*trans*-2-methoxy-cyclopropane-*cis*-3-carboxaldehyde (**2**), together with a small amount of 1-cyano-*cis*-2-methoxy-cyclo-

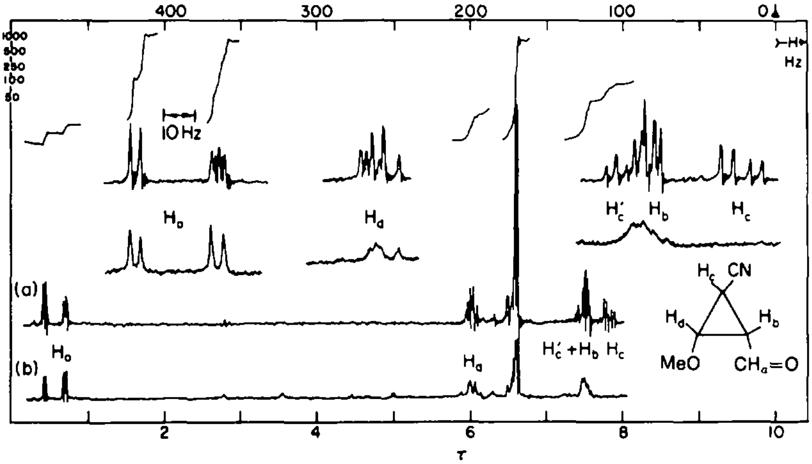
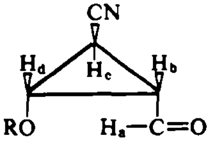


Fig 1. 100 MHz NMR spectrum of the photoadducts, 1-cyano-2-methoxycyclopropane-3-carboxaldehydes in $CDCl_3$: (A) MeOH-Adducts: the integral lines belong to these adducts, and from the lines of H_a in the expanded scale the isomer ratio 1:2:3 is obtained to be 0·52:0·39:0·09; (B) MeOD-Adducts: small impurity peaks at τ 3·55(d), 4·48(s), 5·00(d), 6·5(m) belong to the thermally rearranged product, *trans*-2-hydro-2-methoxy-3-cyano-3-deuterofuran.



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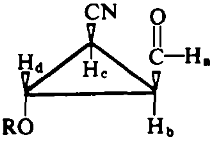

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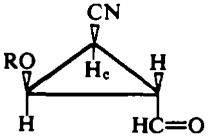

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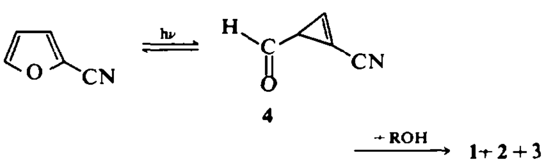
R: Me, Et, or Me_3C

propane-*trans*-3-carboxaldehyde (3). The aldehyde hydrogen, H_a, of (2) is coupled with H_b as well as with H_c through the "W" rule,[10] whereas the interaction between H_a and the OMe group in 1 inhibits the "W" rule coupling between H_a and H_d. In the NMR spectrum of the CH_3OD-adduct, the composite signal of the triplet and the doublet at τ 0·72 is replaced with a single doublet (J = 4·0 Hz), as shown in Fig 1B, due to the loss of the H_a and H_c coupling. The downfield shift of the aldehyde hydrogen of 1 from the one of 2 and of 3 can be attributed to the effect of the neighboring OMe group, characteristic to this structure. The multiplet at τ 6·0 is replaced with a triplet in the MeOD-adducts spectrum, and it clearly belongs to H_d.* There are two distinct, large singlets of the OMe groups of 1 and 2 at τ 6·60 and 6·62. Among the complex multiplet signals at τ 7·5, downfield peaks and the quartet at τ 7·8 belong to H_c, as indicated by the signal loss in the MeOD-adducts spectrum: the rest of the multiplet at τ 7·5 belongs to H_b. Because of a complex four spins system, composed of two main isomeric species, further analysis of the spectrum is not carried out. The irradiation of 2-cyanofuran in ethanol and t-butyl alcohol yields the adducts with the same NMR spectrum except the OMe group signal, which is replaced with the corresponding alkoxy group signals. However, with increase of the size of the alkoxy group, it becomes more difficult to purify the cyclopropane-carboxaldehydes from the photolyzate.

Because only 1-alkoxy-2-cyano-cyclopropane-3-carboxaldehydes were formed in the photolysis of 2-cyanofuran in an alcoholic solution, the primary photochemical reaction is concluded to be the ring contraction to yield 1-cyano-cyclopropene-3-carboxaldehyde 4:



The C=C double bond of 4, conjugated with a cyano group, adds alcohols readily and results in formation of 1, 2, and 3. This addition is regarded as an extended Michael's reaction.[11] Absence of steric hindrance clearly is a major factor favoring formation of 1 and 2 versus 3 and 1-cyano-*cis*-2-methoxy-cyclopropane-*cis*-3-carboxaldehyde, which is probably not formed due to overcrowding in one

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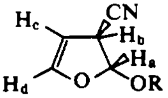
*Among the H_d multiplet, the highest field single peak may be an impurity signal.

side of the cyclopropane ring. Several times repeated experiments are carried out to find any formation of 3-cyanofuran, but even its trace amount is not found among the products in the liquid phase photolysis, in contrast to 2-alkylfuran which photorearranges to 3-alkylfuran.[12]

Thermal rearrangements of photoadducts

When the photoproducts are separated in a gas chromatograph, cyclopropanecarboxaldehydes are barely detected, but 2-alkoxy-*trans*-3-cyano-2,3-dihydrofuran **5** is obtained as the major product with a small amount of its *cis*-isomer **6**. The ratio of *trans*- to *cis*-isomers depends on the size of the alkyl group: 10 for methyl and 20 for ethyl; no *cis*-isomer for t-butyl.



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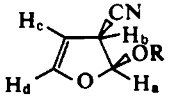

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Quantum and chemical yields of 2-methoxy-*trans*-3-cyano-2,3-dihydrofuran measured with the gas chromatography are 0·062 and 0·26 respectively, when 4×10^{-3} mol l^{-1} 2-cyanofuran solution in methanol is irradiated with a low pressure mercury lamp with intensity 1×10^{17} quanta sec^{-1}. Partial decomposition of the cyclopropanecarboxaldehydes inside the gas chromatograph is responsible for a rather low yield of the dihydrofuran.

Pyrolysis of the photoadducts in a sealed tube confirms the rearrangement inside the gas chromatograph: 10 min heating at 130° and at gas density $8{\cdot}0 \times 10^{-5}$ mol cc^{-1} in a sealed tube completes 94% of the rearrangement of the MeOH-adducts, as shown by Fig 2A, the NMR spectrum of the resulting mixture, which matches the spectrum of the mixture of 90% 2-methoxy-*trans*-3-cyano-2,3-dihydrofuran and 10% its *cis*- isomer. The assignment of the NMR spectrum is shown in the figure. The isomer iwth a larger coupling constant, 7 Hz, between H_a and H_b is assigned *cis*-, and the one with a smaller coupling constant, 3 Hz, *trans*-configuration, because all reported coupling constants for the *cis*-isomers of 2,3-disubstituted-2,3-dihydrofurans are larger than those of the *trans*-isomers.[13] The same ratio of *cis*- and *trans*-isomers for the products **5**, **6** (ratio: 0·10) and the precursors **1**, **2**, **3** (ratio: 0·09) within the experimental error indicates no *cis-trans*- isomerizations of the cyclopropane ring below 130°, thus a concerted process for the ring expansion reaction in the vapor phase.

Spectroscopic data of 2-ethoxy-, and 2-t-butoxy-, 3-cyano-2,3-dihydrofuran are summarized in Table 1. The main mass spectrum peaks of 2-methoxy-3-cyano-2,3-dihydrofuran appear at *m/e* 125 (relative intensity 0·62), 110(0·36), 96 (parent peak 1·00), 94(0·53), 93(0·25), 82(0·64), 66(0·63), 55(0·78), 39(0·72), 31(0·19), 29(1·00). The similarity of the fraction pattern to the one of the cyclopropanecarboxaldehydes reported earlier indicates that the reverse reaction takes place inside the ionization chamber.* Thermal and photochemical rearrangements of dihydrofurans to cyclopropanecarboxaldehydes are well known reactions.[14, 12a,b]

The liquid phase thermal rearrangement of 2-methoxy-3-cyano-2,3-dihydrofuran in a deuterated

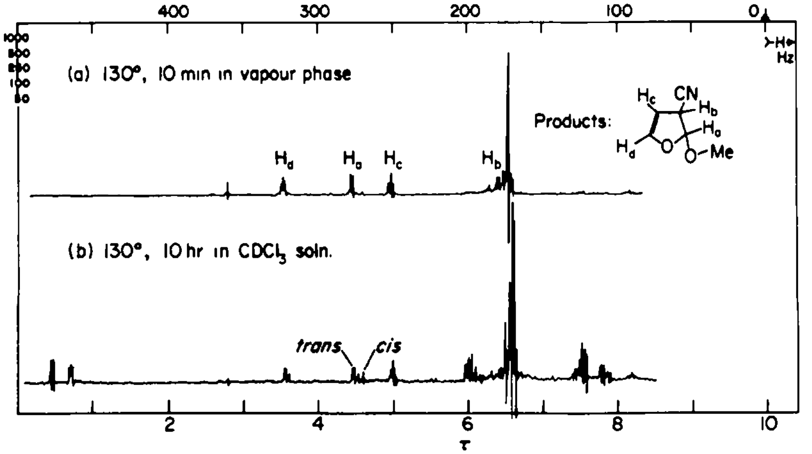

Fig 2. 100 MHz NMR spectrum of thermally rearranged products of 1-cyano-2-methoxy-cyclopropane-3-carboxaldehydes: (A) After 10 min at 130° in the vapor phase; 94% of the original aldehydes disappeared, yielding 2-methoxy-3-cyano-2,3-dihydrofurans with *cis*- to *trans*-ratio = 0·10; (B) after 10 hr at 130° in a $CDCl_3$ solution; 37% conversion; *cis*- to *trans*-ratio = 0·50.

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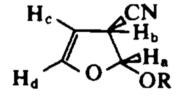
*Hitachi Perkin-Elmer Model RMS-4 Mass Spectrometer: the temperature and the pressure inside the ionization chamber are 200°C and ~ 10^{-6} torr respectively.

Table 1. Summary of spectroscopic data of *trans*- and *cis*-2-alkoxy-3-cyano-2, 3-dihydrofurans



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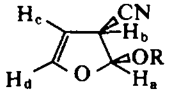

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R		C_2H_5 (5)	$C(CH_3)_3$ (5)	C_2H_5 (6)
NMR in CCl_4, τ	H_a	4·30(d, 1)	4·35(d, 1)	4·40(d, 1)
	H_b	6·42(q, 1)	6·60(m, 1)	6·2(m, 1)
	H_c	4·92(t, 1)	5·20(t, 1)	4·90(t, 1)
	H_d	3·44(t, 1)	3·80(t, 1)	3·48(t, 1)
	CH_2	6·23(q, 2)	————	6·25(q, 2)
	CH_3	8·75(t, 3)	8·74(s, 9)	8·70(t, 3)
	J	$J_{cd} = J_{bc} = J_{bd} = J_{ab} = 3$ Hz		$J_{cd} = J_{bc} = J_{bd} = 3$ Hz, $J_{ab} = 7$ Hz.
IR in CCl_4, cm^{-1}		3000 1370	3000 1350	2990 1340
		2920 1200	2230 1100	2920 1140
		2230 1105	1610 1055	2250 1055
				1620 1010
		1620 1060	1380	1370
Mass, *m/e*		139 93	167 65	139 93
		110 82	137 58	110 82
		109 81	93 56	109 81

chloroform solution was studied in a sealed NMR tube. The typical NMR spectrum obtained is shown in Fig 2B. The rate of the rearrangement is slowed down substantially in the liquid phase, as shown by comparison with Fig 2A. Furthermore, the yield of the *cis*-isomer, 6, is relatively high: relative ratio of *cis*-to *trans*-isomers is 0·50 at 37% conversion after 10 hr heating at 130°, and 0·44 at 32% conversion after 5·2 hr at 158°, in contrast to the vapor phase products ratio 0·10. The *cis*-isomer probably rearranges at a faster rate than its *trans*-isomer because of its additional strain caused by the neighboring functional groups, resulting a relatively large ratio of *cis*-isomer in the early stage of the reaction. Another possible reason is a partial *cis-trans* isomerization in the intermediate state, a α cleaved dihydrofuran biradical: the rate of the ring expansion is in the order of 1/100 of the rate of vapor phase reaction at the same temperature,* leading to a larger possibility of *cis-trans*-isomerization. A prolonged heating of the solution in order to have a high conversion of the methoxy-cyclopropanecarboxaldehyde was inhibited because of black powder formation inside the NMR tube. However, heating 1-cyano-2-*ethoxy*-cyclopropane-3-carboxaldehyde in a deuterated chloroform solution for 3·0 hr at 117° converted 85% of the aldehyde to the dihydrofuran (yield: 72%) with the *cis*- to *trans*-ratio 0·22, in comparison with a gas phase products ratio 0·05. This result supports the latter explanation, that is, a partial *cis-trans*-isomerization in deuterated chloroform in the biradical intermediate state. The ethoxy-cyclopropanecarboxaldehyde rearranges to the dihydrofuran at a rate, $1{\cdot}54 \times 10^{-4}$ sec^{-1} at 117°, 8·6 times faster than the methoxy compound at the same temperature. A similar acceleration of reactions by increased size of substituents is observed in the ring expansion reactions of vinylcyclopropanes to cyclopentenes.[15]

So far the ring expansion rearrangements of the photoadducts, the cyclopropanecarboxaldehydes, are reported. The resulted dihydrofurans, however, are not stable under some conditions. When 2-alkoxy-3-cyano-2,3-dihydrofurans are heated in an aqueous methanol solution between 100 and 187° for a few hr in a sealed, heavy-wall Pyrex tube, only 3-cyanofuran is quantitatively formed. This result is reasonably explained by assuming as an intermediate species 2-hydroxy-3-cyano-2,3-dihydrofuran, which readily loses water to yield 3-cyanofuran.† The unimolecular removal of alcohol

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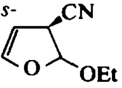
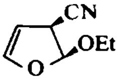
*The correct measurement of the rate of the ring expansion rearrangements in the vapor phase is difficult: main troubles are time lapse for temperature equilibration, and low vapor pressure of the cyclopropanecarboxaldehydes at temperatures convenient for the measurements.

†2-Hydroxy-2,3-dihydrofuran has never been reported as a stable species in the literature.

is too slow to be important in this temperature range, while the above liquid phase reaction is finished after 100 min at 187° with no trace of dihydrofurans remaining.

Vapor phase thermal reactions of 2-ethoxy-3-cyano-2,3-dihydrofurans were studied between 187 and 415°. From *trans*-2-ethoxy-3-cyano-2,3-dihydrofuran, its *cis*-isomer, 3-cyanofuran, ethanol and a trace of an aldehyde are formed. From the *cis*-dihydrofuran, its *trans*-isomer, 3-cyanofuran, ethanol and the aldehyde are obtained. Typical results are shown in Table 2. We have not determined the exact structure of the aldehyde because of its small yield, but it had IR bands (2810, 2700, 1725 cm^{-1}) characteristic of an aldehyde, the same molecular weight as the starting dihydrofuran. Pyrolyses of other 2-alkoxy-3-cyano-2,3-dihydrofurans proceed analogously to the ethoxy compounds.

Table 2. Typical results of vapor phase pyrolysis of 2-ethoxy-3-cyano-2, 3-dihydrofurans

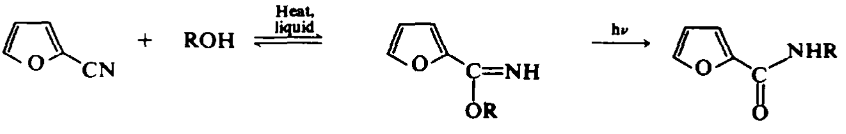
		Initial rate of formation, sec^{-1}			
Initial species	Temp °C	*trans*-isomer	*cis*-isomer	3-Cyanofuran	Aldehyde
trans- 	187	------------	$3{\cdot}1 \times 10^{-7}$	$2{\cdot}5 \times 10^{-7}$	$6{\cdot}7 \times 10^{-8}$
	340	------------	$8{\cdot}9 \times 10^{-7}$	$1{\cdot}2 \times 10^{-5}$	------------
cis- 	340	$1{\cdot}6 \times 10^{-5}$	------------	$1{\cdot}1 \times 10^{-5}$	$1{\cdot}8 \times 10^{-6}$

Thermal addition of alcohols to 2-cyanofuran

In order to find out whether formation of 2,3-dihydrofurans can take place only photochemically, we studied the thermal addition of alcohols to 2-cyanofuran and 3-cyanofuran between 100 and 200° under pressure in sealed tubes. 3-Cyanofuran does not yield any thermal adducts with alcohols even after 35 hr at 200°, whereas 2-cyanofuran yields quantitatively 1-methoxy-1-(2-furan)-methylemimine 7 with 75% conversion after 8 hr at 187°. The surface of the reactors (Pyrex, Pyrex treated with a sodium hydroxide solution, or brass tubes) does not have any effect on the reaction. Ethanol does not yield the thermal adduct as effectively as methanol does: after 8 hr at 187°, 50% of the original 2-cyanofuran has reacted to yield 1-ethoxy-1-(2-furan)-methylenimine (yield: 40%), 2-furoic acid methyl ester (40%), and 2-furoic acid (7%). t-Butyl and isopropyl alcohols do not yield stable thermal adducts. Spectroscopic data of the adducts are summarized in Table 3. In the adduct formed with MeOD, the broad NMR band due to the proton of the imine group at τ 2·3 is absent, with the rest of the spectrum unchanged. The thermal reaction does not yield any trace of the photochemical adducts, i.e., the substituted, 2,3-dihydrofurans. The vapor phase pyrolysis of 1-methoxy-1-(2-furan)-methylenimine at 300° yields 2-cyanofuran and methanol as major products. Its vapor phase photolysis with low pressure mercury lamps primarily yields 2-furyl-methylamino-ketone **8**, with small amounts of 2-cyanofuran and methanol. All these results confirm the molecular structure of the thermal adducts.

DISCUSSION

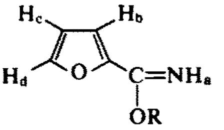
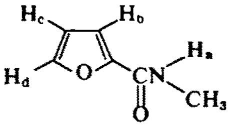
The primary photochemical process of 3-substituted furans is the bond breakage between the oxygen in the ring and the 5-carbon next to the oxygen to yield 3-substituted cyclopropene-3-carboxaldehydes **9**, whereas the 2-substituted furans yield 1-substituted cyclopropene-3-carboxaldehydes **10**.[12] In order for the Michael's reaction to take place, the substituent group must be in the same plane with the cyclopropene ring. This can be accomplished in **10**, but not in **9**, thus explaining why 3-cyanofuran did not yield the photoaddition products. The same primary process explains the

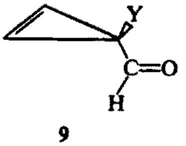


7 **8**

R: Me(7, 8), Et(7).

Table 3. Summary of spectroscopic data of 1-alkoxy-1-(2-furan)-methylenimine 7, and 2-furyl-methylamino-ketone 8

		 7		 8
	R	CH_3	C_2H_5	CH_3
NMR in CCl_4	H_a	2·30(broad)	2·20(broad)	3·8(broad)
	H_b	3·41(d, 1)	3·29(d, 1)	2·87(d, 1)
	H_c	3·67(q, 1)	3·52(q, 1)	3·50(sextet, 1)
	H_d/R	2·63(q, 1)	2·48(q, 1)	2·55(m, 1)
	CH_2	--------------------	5·67(q, 2)	--------------------
	CH_3/OCH_3	6·21(s, 3)	8·65(t, 3)	6·99(d, 3)
	J	$J_{cb} = 3$ Hz	$J_{cb} = 3·7$ Hz $J_{cd} = 3$ Hz	$J_{NK-CH_3} = 5$ Hz $J_{cb} = 3·5$ Hz
IR in CCl_4, cm^{-1}		3300 (νN—H)	3320	3390
		2980	2980	2900
		2910	1650 (νC=N)	1680 (νC=O)
		1650 (νC=N)	1550	1600
		1550	1330	1290
		1350	1080	
		1090	1000	
		1020		
		965		
Mass, *m/e*		125	139	125
		95		111
		94		95
		81		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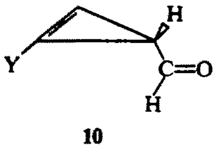
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specific behavior of photoisomerizations and photodecarbonylations of furans.[12c,*]

The absence of 3-cyanofuran among the photoproducts can be explained by a strong inductive effect of the cyano group in the cyclopropene ring, so that only reverse reaction to 2-cyanofuran and the Michael's alcohol addition took place, while an alkyl group as a substituent to the cyclopropene ring does not have such a strong effect, resulting in rearrangement to 3-alkylfuran and non-addition of alcohols to the cyclopropene ring.

EXPERIMENTAL

1-Cyano-2-methoxy-cyclopropane-3-carboxaldehydes, **1**, **2**, *and* **3**.

Preparation. As a typical example, 1·0 g purified 2-cyanofuran and 80 g anhyd MeOH were mixed together in an immersion type photoreactor with a low pressure mercury lamp (intensity at 254 nm: 1×10^{17} quanta/sec). After the soln was completely deaerated under a vacuum, the soln was irradiated for 12 hr at 0°. The solvent was completely removed with a rotary evaporator at a reduced pressure. The remaining viscous yellowish liquid 1·2 g was placed inside a high vacuum system, and transferred from a trap to a cold trap at −60° by warming the liquid instantaneously by a heat gun at 10^{-2} torr pressure. The transfered pale yellowish liquid is a mixture of 1-cyano-2-methoxy-cyclopropane-3-carboxaldehydes and 2-methoxy-3-cyano-2,3-dihydrofurans as minor components. In order to remove the latters, the liquid was warmed to 50° under 10^{-3} torr vacuum for 10 min. The remaining viscous liquid 0·3 g (22% yield) is free from 2-methoxy-3-cyano-2,3-dihydrofurans. Other 1-alkoxy-2-cyano-cyclopropane-3-carboxaldehydes were prepared in an analogous way.

Vapor phase thermal rearrangements. 10 μl purified 1-cyano-2-methoxy-cyclopropane-3-carboxaldehyde was sealed in a Pyrex glass tube (50 ml in volume) at a pressure below 10^{-4} torr. The entire tube was then submersed in a constantly boiling liquid. After some time of heating, the tube was taken out and cooled to −60°. Through a narrow broken seal, 0·5 ml of $CDCl_3$ was added to dissolve all the soluble compounds inside the tube, and then transferred to an NMR tube for the spectrum measurement with Varian HA-100 MHz Spectrometer.

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[*] As an exception, 2-furfuraldehyde in methanol quantitatively yields 2-furyldimethoxymethane upon irradiation at 254 nm.

Liquid phase thermal rearrangements. 20 μl pure 1-cyano-2-methoxy-cyclopropane-3-carboxaldehydes and 0·5 ml $CDCl_3$ were put together with a small amount of TMS in an NMR tube and sealed in a high vacuum. The entire tube was then submersed in a constantly boiling liquid, and periodically taken out for the NMR measurement. The $CHCl_3$ peak was taken as a standard for a rate measurement.

2-*Methoxy*-3-*cyano*-2,3-*dihydrofurans*

Preparation. As a typical example, 260 ml methanol soln containing 0·13 g 2-cyanofuran was placed in an immersion type photoreactor with a low pressure mercury lamp (intensity at 254 nm: 1×10^{-5} Einstain min^{-1}), and the soln was deaerated under a vacuum. After 5 hr irradiation, the solvent was removed at a reduced pressure, and the condensed soln was injected into Hewlett-Packard Research Chromatograph Model 5750 with an 8 feet long 550X Ucon oil column (200° injection port temp, 240° TC and outlet ports temp, 60 ml min^{-1} flow rate). At a 2°C min^{-1} programmed rate, starting at 125 to end at 180°, 2-cyanofuran 0·065 g was recovered 4·0 min after injection, and *trans*-2-methoxy-3-cyano-2,3-dihydrofuran 0·023 g and its *cis*-isomer 0·002 g were obtained 10·0 and 24·2 min after injection respectively. The products obtained in thermal rearrangements of 1-cyano-2-methoxy-cyclopropane-3-carboxaldehydes appeared at the same retention times and had the same spectroscopic data as the ones mentioned above.

Thermal reactions in aqueous methanol solutions. 0·050 g 2-methoxy-3-cyano-2,3-dihydrofuran, 2·0 g water, and 3 ml MeOH were mixed together and sealed in a heavy wall Pyrex glass tube under a vacuum. After heating for 100 min in a constantly boiling liquid at 187°, the tube was cooled, and the soln was injected to the gas chromatograph. After MeOH and water peaks, 3-cyanofuran 0·045 g appeared 10·0 min after injection at a 125° constant temp run, with no trace of 2-cyanofuran which had a retention time 8·5 min at this condition. The NMR spectrum of 3-cyanofuran: τ^{CCl_4} 2·05(m, 1), 2·49(m, 1), 3·35(m, 1).

Pyrolysis of 2-*methoxy*-3-*cyano*-2,3-*dihydrofuran.* 2-Methoxy-3-cyano-2,3-dihydrofuran 12 μl (10^{-4} mol) was sealed in a 24·4 ml Pyrex glass tube at a pressure below 10^{-4} torr, and it was placed inside a furnace. After heating, typically 3 hr at 349°, the tube was cooled and the entire content was injected into the gas chromatograph through a break seal. The results are shown in Table 2.

Thermal addition of methanol to 2-*cyanofuran.* Purified 2-cyanofuran 0·50 g and 3·0 g MeOH were mixed together and sealed in a heavy wall Pyrex glass tube in a vacuum. After heating for 8 hr at 187°, the soln was injected to the gas chromatograph. At a 2° min^{-1} programmed rate starting to 100° to end at 180°, 2-cyanofuran 0·12 g was recovered, and 1-methoxy-1-(2-furan)-methylenimine 0·50 g was obtained 18·5 min after injection.

Vapor phase photolysis of 1-*methoxy*-1-(2-*furan*)-*methylenimine.* The imine 0·20 g was placed inside an 800 ml quartz tube, and the tube was pumped out to 10^{-4} torr at 77° K. The tube was then placed inside another quartz tube partially wrapped with heated nichrom wire. After temp equilibration at 200°, the irradiation was carried out with a surrounding bank of low pressure mercury lamps. The whole content of the tube was then injected into the gas chromatograph with a 6 feet Apiezone oil column. In a 2° min^{-1} programmed rate starting at 100° to end 180°, 2-furyl-methylamino-ketone 0·030 g was obtained 30 min after injection. In addition, 2-cyanofuran and methanol were obtained as products, but quantitative results were hard to obtain because of the very low vapor pressure of the main product.

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