REACTION OF PHENYLCHLOROCARBENE WITH 2-ALKENYLFURANS AND SOME TRANSFORMATIONS OF THE FORMED ADDUCTS*

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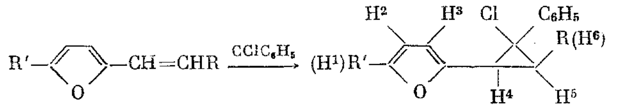
Previously we had shown that dihalocarbenes react with 2-alkenylfurans to give mainly adducts at the olefinic bond [4], whereas ethoxycarbonylcarbene, which is generated thermocatalytically from ethyl diazoacetate, preferentially attacks the unsubstituted double bond of the furan ring (FR) [5]. In the present paper we studied the reactions of 2-vinylfuran (Ia) and its homologs (Ib)-(Id) with phenylchlorocarbene, and also the transformations of the formed adducts under the influence of Na solutions in NH_3 at -60°, and of H_2 in the presence of Pt/C at 230-310°.

It proved that phenylchlorocarbene, which is generated by the action of $t\text{-}C_4H_9OK$ on $C_6H_6CHCl_2$, reacts with (I) to give the corresponding chlorophenylfurylcyclopropanes (II).



(I) (II)

$R=R'=H$ (a); $R=CH_3$, $R'=H$ (b); $R=H$, $R'=CH_3$ (c); $R=R'=CH_3$ (d)

At 80-100° the yields of (II) were 30-40%, and only 5-7% at ~20°. Since $CClC_6H_5$ is an unsymmetrical singlet carbene, the formed (II) adducts represented mixtures of the corresponding cis and trans isomers.† The composition and structure of the (II) adducts were established on the basis of the GLC, elemental analysis, IR, mass, and NMR spectral data (Table 1).

The NMR spectrum of 1-chloro-1-phenyl-2-(2-furyl)cyclopropane (IIa), obtained from vinylfuran (Ia), represented a superimposition of the spectra of the cis and trans isomers. The H^1 signals of the FR are masked by the signals of the benzene protons of both isomers to give a complex multiplet at δ 7.05 ppm. Two AB spectra correspond to the H^2 and H^3 protons, with centers at 6.08 for the cis and 5.65 ppm for the trans isomer. A doublet of doublets, with δ 2.75 ppm, corresponds to the H^4 proton of the CPR in the trans isomer ($J_{H^4H^5} = 4.7$ Hz, $J_{H^4H^6} = 3.8$ Hz). The methylene protons of the CPR (H^5 and H^6) of the cis and trans isomers give a multiplet at 1.75 ppm. A distinct difference in the signals of the H^2, H^3, and H^4 protons for the cis and trans isomers of (IIa) made it possible to determine that their ratio was 1:2.1, which was in exact agreement with the GLC data.

The NMR spectrum of 1-chloro-1-phenyl-2-methyl-3-(2-furyl)cyclopropane (IIb), the same as the GLC data, indicated that it contained the cis and trans isomers in a 1:2 ratio.‡ The complex multiplet

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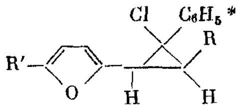
*The preliminary results are given in [1, 2]; also see [3].

†Here and subsequently the cis and trans isomers are, respectively, the adducts with a cisoid or a transoid arrangement of the furyl and phenyl substituents in the cyclopropane ring (CPR).

‡The formation of four isomers is possible in this case, since the starting 2-propenylfuran (Ib) represented a mixture of the configurational isomers (40:60). However, we were unable to detect all of the possible isomers of (IIb) employing NMR and GLC.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 379-384, February, 1976. Original article submitted March 28, 1975.

TABLE 1. Properties of Furyl-gem-phenylchlorocyclopropanes 

Compound	R	R′	Yield, %	Bp, °C (p, mm of Hg)	n_D^{20}	Found, %			Empirical formula	Calculated, %			Data of IR spectra (ν, cm^{-1})
						C	H	Cl		C	H	Cl	
(IIa)	H	H	31	82—84(1)	1,5653	71,51	5,08	16,62	$C_{13}H_{11}ClO$	71,41	5,03	16,23	894, 1508, 3120 (FR) 702, 742, 757 (C—Cl) 1021, 1055, 3080 (CPR) 1455, 1515, 1605, 3030 (C_6H_5)
(IIb)	CH_3	H	34	86—87(1)	1,5601	72,40	5,70	14,99	$C_{14}H_{13}ClO$	72,24	5,62	15,25	885, 1505 (FR); 700, 735, 747 (C—Cl) 1012, 1025, 3085 (CPR); 1442, 1592, 3030 (C_6H_5) 1380 (CH_3)
(IIc)	H	CH_3	30	94—96(1)	1,5531	72,48	5,63	15,16	$C_{14}H_{13}ClO$	72,24	5,62	15,25	889, 1500, 3110 (FR) 703, 759, 790 (C—Cl) 1007, 1045, 3040 (CPR); 1450, 1572, 3028 (C_6H_5) 1385, 2975 (CH_3)
(IId)	CH_3	CH_3	31	112—116(1)	1,5532	72,84	5,97	14,12	$C_{15}H_{15}ClO$	73,00	6,12	14,38	905, 1498, 3115 (FR) 702, 760, 787 (C—Cl) 1022, 1050, 3068 (CPR), 1450, 1576, 1620, 3035 (C_6H_5) 1380 (CH_3)

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*The data of the NMR spectra are given in the text.

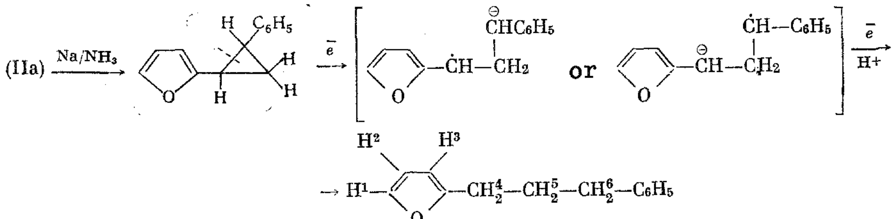
at δ 7.1 ppm corresponds to the H^1 protons of the FR and C_6H_5 group. The multiplet at 6.1 ppm corresponds to the H^2 and H^3 protons of the cis isomer. The H^2 and H^3 protons of the trans isomer, respectively, give multiplets with δ 5.85 and 5.45 ppm. A multiplet at 2.21 corresponds to the H^4 proton of cis-(IIb), while in the case of trans-(IIb) the multiplet is found at 1.83 ppm. The protons of the CH_3 group and H^5 give in the spectrum the AB part of the ABX system in the 0.7-1.5 ppm region.

Based on the GLC and NMR spectral data, the 1-chloro-1-phenyl-2-(5-methyl-2-furyl)cyclopropane (IIc), formed from 2-vinyl-5-methylfuran (Ic), represented a mixture of the cis and trans isomers in a 40 : 60 ratio. The phenyl protons give in the spectrum a complex multiplet at 7.05 ppm. Two groups of lines correspond to the protons of the FR (H^2 and H^3), at 5.80 for cis-(IIc) and 5.38 ppm for trans-(IIc). The H^4 proton of the trans isomer gives a doublet of doublets at 2.70 ppm, with a spin–spin coupling constant [SSCC] of 9.5 Hz, and distant splitting of each line due to coupling of this proton with H^5 and H^6 (J = 7.8 Hz). A triplet at δ 2.40 ppm (J = 9 Hz) corresponds to the H^4 proton of cis-(IIc). The protons of the CH_3 group in the FR give two broad singlets with δ 2.14 and 1.88 ppm for the cis and trans isomers, respectively. A multiplet at 1.67 ppm is observed for the H^5 and H^6 protons.

The mass spectrum of (IIc) has the peak of the molecular ion with m / e 232 (234), and also the peaks of the ions that are characteristic for the fragmentation of furans [6], with m / e 197 ($M^+ - Cl$), 155 ($M^+ - Cl - CH_2CO$), 154 ($M^+ - Cl - CH_3CO$), and 153 ($M^+ - Cl - CH_3CO - H$). In addition, the peak of the ion with m / e 115 is present, which probably has a cyclopropene structure and is formed from the molecular ion via the cleavage of the furyl radical and a molecule of HCl.

Of the four geometric isomers that are possible, in the NMR spectrum of 1-chloro-1-phenyl-2-methyl-3-(5-methyl-2-furyl)cyclopropane (IId) it is possible to establish, the same as in the case of (IIb), the presence of only the cis and trans isomers when based on the phenyl and furyl groups. The signals of the phenyl protons are present downfield (δ 7.10 ppm). A multiplet at 5.81 corresponds to the H^2 and H^3 protons of cis-(IId), and at 5.42 ppm in the case of trans-(IId). The singlets with δ 1.92 and 2.14 ppm belong to the protons of the CH_3 group in the FR of the trans and cis isomer, respectively. The signal of the H^4 proton of both isomers forms a complex multiplet at 2.00 ppm. The protons of the CH_3 group in the CPR of the trans isomer give a nonfirst-order doublet with δ 1.5 ppm (J = 6 Hz), whereas for cis-(IId) this doublet is superimposed on the signals of the methyl protons in the FR. The signal of the H^5 proton of trans-(IId) also represents a nonfirst-order quadruplet with an intrinsic constant of J = 6 Hz. A comparison of the intensities of the signals of the H^2 and H^3 protons of trans and cis (IId) made it possible to establish that their ratio in the obtained specimen was 2.3 : 1.

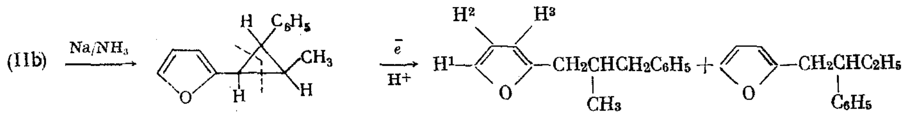
The reduction of adducts (IIa) and (IIb) by Na solutions in NH_3 of variable concentration (ranging from 3.5 to 17%) at −60° was accompanied, in contrast to the furyl-gem-dichlorocyclopropanes [4], by hydrogenolysis of the CPR, which is associated with the greater electron affinity of the diarylcyclopropanes and the higher stability of the anion-radicals and dianions formed from them (cf. [7]). Here the hydrogenolysis of (IIa) proceeded exclusively at the 1,2 bond of the CPR to give 1-phenyl-3-(2-furyl)propane (IIIa) in 65-70% yield.



(IIIa)

The NMR spectrum of (IIIa) has, besides the characteristic signals of the furyl H^1 proton and the protons of the C_6H_5 group at δ 7.05 ppm, and also of the furyl H^2 proton at 6.10 and the H^3 proton at 5.80 ppm, a quintet from the two H^5 protons with δ 1.80 ppm (J = 7.5 Hz), and two distorted triplets of the H^4 and H^6 protons, which in their intensity correspond to the CH_2 groups (δ 2.05 ppm, J = 7.5 Hz).

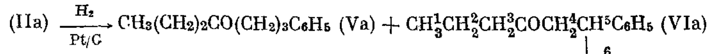
Based on the GLC data, in contrast to (IIa), the reduction of (IIb) using Na / NH_3 led to a mixture of two products in a 3.5 : 1 ratio (total yield ~70%), which were separated by preparative GLC (PGLC). According to the NMR spectra, the compound with the shorter retention time was the hydrogenolysis product at the 1,2 bond of the CPR, and specifically 1-phenyl-2-methyl-3-(2-furyl)propane (IIIb) (yield ~55%), while the compound with the longer retention time was 1-(2-furyl)-2-phenylbutane (IVb), i.e., the product of opening the 1,3 bond in the CPR (yield ~15%).



(IIIb) (IVb)

In particular, the NMR spectrum of compound (IIIb) contains multiplets at 7.1 (H^1) and 7.03 ppm (C_6H_5), two doublets of doublets at 6.07 and 5.83 ppm (H^2 and H^3), a complex multiplet at 2.85-1.8 ppm (CH_2CHCH_2 fragment), and a doublet at 0.74 ppm (CH_3, J = 6.3 Hz).

The catalytic hydrogenation of (II) over 5% Pt / C at 230-310° was accompanied by hydrogenolysis of both the CPR and the furan (tetrahydrofuran) nucleus, and led to phenyl-substituted ketones. Here the complete conversion of (II) was observed at ≥260-265° (at a space velocity of 0.2 h^{-1}). In contrast to the furyl-gem-dichlorocyclopropanes [8], it is characteristic that the hydrogenolysis of the (II) compounds under the same conditions was less selective. Thus, based on the GLC and NMR spectral data, from (IIa) was obtained in an overall yield of 80-90% a mixture of the 1- and 2-phenyl-4-heptanones (Va) and (VIa) in a respective ratio of ~5 : 3.



$$\text{(IIa)} \xrightarrow[\text{Pt/C}]{H_2} CH_3(CH_2)_2CO(CH_2)_3C_6H_5\ \text{(Va)} + CH^1_3CH^2_2CH^3_2COCH^4_2\underset{\displaystyle CH^6_3}{\underset{|}{CH^5}}C_6H_5\ \text{(VIa)}$$

The NMR spectrum of isomer (VIa), which was isolated by PGLC and has the shorter retention time, has 7 groups of lines (δ, ppm): 0.71 t (CH^1_3, $J_{H^1H^2}$ = 7.5 Hz); 1.11 d (CH^6_3, $J_{H^6H^5}$ = 7.0 Hz); 1.39 t.q. (CH^2_2, for the triplet J = 6.8 Hz, for the quadruplet J = 7.5 Hz); 2.08 t (CH^3_2, $J_{H^2H^3}$ = 6.8 Hz); 2.44 d (CH^4_2, $J_{H^4H^5}$ = 7 Hz); 7.05 m (CH^5); 7.20 m (C_6H_5).

The hydrogenolysis of (IIb) under analogous conditions took place at all of the C – C bonds of the CPR, although the opening of the FR, similar to (IIa) and other similar compounds [8], proceeded selectively at the C – O bond, away from the substituent. As a result, a mixture of isomeric ketones (Vb), (VIb), and (VIIb) was obtained in a close ratio (1.5 : 1.6 : 1).

$$\text{(IIb)} \xrightarrow[\text{Pt/C}]{H_2} CH_3(CH_2)_2COCH_2CH(CH_3)CH_2C_6H_5\ \text{(Vb)} + CH_3(CH_2)_2COCH_2CH(C_2H_5)C_6H_5\ \text{(VIb)} + CH_3(CH_2)_2COCH(C_2H_5)CH_2C_6H_5\ \text{(VIIb)}$$

The NMR spectrum of the obtained mixture contains 6 groups of lines: the triplet at δ 0.68 ppm belongs to the methyl protons of the ethyl and propyl radicals of isomers (VIb) and (VIIb); the complex multiplet at 1.40 ppm belongs to the protons of the CH_2 groups adjacent to the CH groups of these compounds; the triplet at δ 2.05 ppm belongs to the protons of the CH_2 groups of the propyl radical, found α to the keto group; the doublet at δ 2.50 ppm belongs to the protons of the CH_2 group attached to phenyl (VIIb) and the CH_2 group of the $COCH_2CHC_6H_5$ fragment (VIb); the quintet with δ 2.94 ppm belongs to the methine protons of the isomeric ketones. In addition, the structure of (Vb) is determined by the more probable direction of opening the three-membered ring of compound (IIb).

Isomers (Vb), (VIb), and (VIIb) were separated by fractional distillation and PGLC; their IR spectra had an intense band in the 1712 cm^{-1} region, which is characteristic for the C = O group.

EXPERIMENTAL METHOD

The GLC analysis was run on an LKhM-8MD chromatograph using a 300 × 0.3 cm column packed with 20% Apiezon L deposited on Chromosorb P (80-100 mesh), or with 15% SKTP-50 deposited on silanized Chromosorb G (60-80 mesh); the carrier gas was helium. The preparative separation was run on a Chrom-3 chromatograph [4 m × 6 mm stainless steel column, 10% SKTP-50 deposited on Chromosorb P (60-80 mesh), 180°, and helium flow rate = 40 ml / min].

The NMR spectra were obtained on a Varian DA-60 IL instrument (60 MHz) using HMDS as the internal standard. The IR spectra were taken on a UR-20 instrument (as a thin layer of the compound). The mass spectra were obtained on a Varian MAT CH-6 instrument, with direct insertion of the sample into the ion source.

The 2-alkenylfurans were obtained in 60-75% yields by the dehydration of the corresponding alkyl-2-furylcarbinols [4].

Preparation of Furyl-gem-phenylchlorocyclopropanes (II). To a stirred suspension of t-C_4H_9OK (from 0.25 g-atom of K) in 250 ml of n-hexane were added 0.5 mole of the 2-alkenylfuran and 0.25 mole of benzal chloride. The stirred mixture was refluxed for 2 h, cooled to ~20°, and hydrolyzed with 250 ml of water. The organic layer and ether extracts (2 × 50 ml) were combined, washed with 300 ml of water, and dried over $MgSO_4$. The n-hexane and ether were distilled off using a rotary evaporator, while the residue was vacuum-distilled. The yields and properties of the obtained (II) adducts are given in Table 1.

Reduction of 1-Chloro-1-phenyl-2-furylcyclopropanes (II) with Sodium in Liquid Ammonia. a) To a stirred 4.7% solution of Na (0.4 g) in 10 ml of NH_3, cooled in a solid CO_2 – acetone mixture (–55 to –60°), was added 2 g of 1-chloro-1-phenyl-2-furylcyclopropane (IIa) in 5 ml of abs. ether in 10 min. Then 2 g of NH_4Cl was added at one time. The excess NH_3 was evaporated through a cooled trap, and the residue was diluted with 10 ml of water and then extracted with ether (2 × 20 ml). After the usual workup and fractional distillation we obtained 1.1 g (66%) of 1-phenyl-3-(2-furyl)propane (IIIa), which was 99.4% pure (based on the GLC data), bp 79-80° (1 mm); n_D^{20} 1.5321. Found: C 83.64; H 7.57%. $C_{13}H_{14}O$. Calculated: C 83.85; H 7.57%. Infrared spectrum (ν, cm^{-1}): 889, 1040, 1500, 3120 (FR); 2869, 2945 (CH_2); 1485, 1510, 1600, 3089 (C_6H_5).

The reduction of (IIa) with a 17% solution of Na in NH_3 gave the same result.

b) To a stirred 11% solution of Na in NH_3 (from 2 g of Na and 20 ml of NH_3) at –55 to –66° was added 3 g of 1-chloro-1-phenyl-2-methyl-3-(2-furyl)cyclopropane (IIb) in 10 ml of abs. ether. The reaction products were worked up in the usual manner, followed by distillation to give 1.7 g (67%) of a mixture of 78% of (IIIb) and 22% of (IVb), bp 81-84° (1 mm), n_D^{20} 1.5272, which was separated by PGLC. 1-Phenyl-2-methyl-3-(2-furyl)propane (IIIb), bp 82-83° (1 mm), n_D^{20} 1.5267. Found: C 83.67; H 7.95%. $C_{14}H_{16}O$. Calculated: C 83.96; H 8.05%. Infrared spectrum (ν, cm^{-1}): 890, 1037, 1505, 3112 (FR); 1458, 1598, 3030, and 3085 (C_6H_5). 1-(2-Furyl)-2-phenylbutane (IVb), bp 83-84° (1 mm). Found: C 83.59; H 7.92%. $C_{14}H_{16}O$. Calculated: C 83.96; H 8.05%.

In a similar experiment, run with 5.4% Na/NH_3 solution (from 0.7 g of Na and 12.2 g of NH_3), from 3 g of (IIb) we obtained 1.8 g (71%) of a mixture of (IIIb) and (IVb) in a 2.1 : 1 ratio.

Hydrogenation of 1-Chloro-1-phenyl-2-furylcyclopropanes (II). a) 1-Chloro-1-phenyl-2-(2-furyl)-cyclopropane (IIa) (6 g) was passed at a space velocity of 0.2 h^{-1} in excess H_2 through a quartz tube, containing 5% Pt/C, at 260-265°. The catalyzate was neutralized with potash, separated from the water, dried, and then vacuum-distilled, bp 86-88° (1 mm). We isolated 4.5 g (86%) of a mixture of 1-phenyl-4-heptanone (Va) and 2-phenyl-4-heptanone (VIa) (5 : 3 ratio), which was separated by PGLC. Ketone (Va) has a shorter retention time and its purity was 98% (based on the GLC data); n_D^{20} 1.5016. Found: C 82.11; H 9.57%. $C_{13}H_{18}O$. Calculated: C 82.05; H 9.53%. Infrared spectrum (ν, cm^{-1}): 1715 (C = O); 1465, 1500, 1602, 3030 (C_6H_5); 1385, 2975 (CH_3). Compound (VIa) had a purity of 93% [the remainder was (Va)]; n_D^{20} 1.5025. Found: C 81.92; H 9.66%. $C_{13}H_{18}O$. Calculated: C 82.05; H 9.53%. Infrared spectrum (ν, cm^{-1}): 1715 (C = O); 1465, 1505, 1603, 3030 (C_6H_5); 1387 (CH_3).

b) Six grams of 1-chloro-1-phenyl-2-methyl-3-(2-furyl)cyclopropane (IIb) was hydrogenated under the above-indicated conditions. From the catalyzate after the usual workup and fractional distillation we obtained 4.3 g (81%) of a mixture with bp 87-92° (1 mm), n_D^{20} 1.4986, which consisted of 1-phenyl-2-methyl-4-heptanone (Vb), 3-phenyl-5-octanone, and 3-benzyl-4-heptanone (VIIb) in a 1.5 : 1.6 : 1 ratio (based on the GLC data). The mixture was separated by fractional distillation in vacuo and subsequent PGLC.

Compound (VIb), purity 99.8%, bp 92° (1 mm); n_D^{20} 1.4981. Found: C 82.34; H 9.92%. $C_{14}H_{20}O$. Calculated: C 82.30; H 9.86%. Infrared spectrum (ν, cm^{-1}): 1712 (C = O); 1490, 1603, 3070, 3091 (C_6H_5); 1380, 1465, 2968 (CH_3). Compound (Vb), purity 95%, bp 87-88° (1 mm); n_D^{20} 1.4974. Compound (VIIb), purity 93% [the remainder was (Vb) and (VIb)]; n_D^{20} 1.4971. The IR spectra of (Vb) and (VIIb) contain an intense band at 1712 cm^{-1}. The NMR spectral data for compounds (III)-(VII) are given in the text.

CONCLUSIONS

1. 2-Alkenylfurans react with phenylchlorocarbene to give furyl-gem-phenylchlorocyclopropanes.

2. Reduction of the furyl-gem-phenylchlorocyclopropanes with sodium in liquid ammonia leads to hydrogenolysis of the cyclopropane ring with the formation of 1-furyl-3-phenylalkanes.

3. The catalytic hydrogenation of the furyl-gem-phenylchlorocyclopropanes in a flow system over Pt/C at 260-265° leads to hydrogenolysis of both the furan and cyclopropane rings with the formation of phenyl-substituted ketones.

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