STUDY OF FURAN COMPOUNDS

XLVII* DIENE SYNTHESIS ON THE BASIS OF 2,5-DIMETHOXY-2,5-DIHYDROFURAN AND 2-METHOXY-7-METHYL-1,6-DIOXASPIRO[4.4]-3-NONENE

A. A. Ponomarev, I. A. Markushina,
and G. E. Marinicheva

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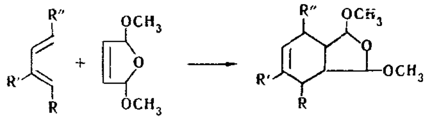
Adducts of 2,5-dimethoxy-2,5-dihydrofuran with several dienes were obtained by the Diels-Alder reaction. The possibility of the participation of 2-methoxy-7-methyl-1,6-dioxaspiro-[4.4]-3-nonene as a dienophile in the diene synthesis was demonstrated for the first time. The structures of the adducts were confirmed by their IR spectra and catalytic hydrogenation.

It is well known that 2,5-dihydrofurans can be used as one of the components in the Diels-Alder reaction [1,2]. We have investigated the reaction of 2,5-dimethoxy-2,5-dihydrofuran (I) and 2-methoxy-7-methyl-1,6-dioxaspiro[4.4]-3-nonene (II) with various dienes. The adducts obtained are of interest for the synthesis of the little studied compounds of the 4,7-dihydro- and 4,5,6,7-tetrahydroisoindole series [3].

Compound I was condensed with butadiene, piperylene, isoprene, and 1,2- and 1,4-dimethyl-1,3-butadiene at 200 deg C.

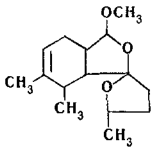
A mixture of the diene and dienophile (2 : 1) was heated for 13-15 h in the presence of a small amount of hydroquinone.



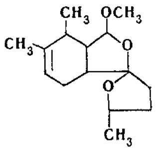
III-VII

R, R′, R″ = H III; R = CH_3; R′, R″ = H IV; R, R″ = H; R′ = CH_3 V; R, R′ = CH_3; R″ = H VI; R, R″ = CH_3; R′ = H VII

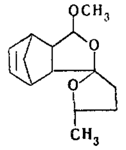
Adducts VIII and IX were similarly obtained by the reaction of II with 1,2-dimethyl-1,3-butadiene and cyclopentadiene; adduct VIII, owing to the unsymmetrical structure of the diene and dienophile, can exist as one or two assumed forms (VIIIa and VIIIb).



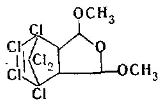
VIIIa



VIIIb



IX



X

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*See [8] for Communication XLVI.

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TABLE 1. Adducts from the Diene Synthesis

Compound	Diene	Dienophile	Bp or Mp, °C (press., mm)	n_D^{20}	d_4^{20}	MR_D	
						Found	Calc.
III	Butadiene	I	76—80 (3)	1,4769	1,066	48,87	48,44
IV	Piperylene	I	78—86 (2)	1,4730	1,063	53,55	53,06
V	Isoprene	I	91—100 (3)	1,4745	1,048	53,25	53,06
VI	1,2-Dimethyl-1,3-butadiene	I	102—112 (7)	1,4750	1,029	58,08	57,68
VII	1,4-Dimethyl-1,3-butadiene	I	83—90 (3)	1,4720	1,031	57,68	57,68
VIII	1,2-Dimethyl-1,3-butadiene	II	100—108 (1)	1,4881	1,032	69,76	69,33
IX	Cyclopentadiene	II	123—130 (3)	1,5000	1,106	62,82	62,51
X	Hexachlorocyclopentadiene	I	161—162	—	—	—	—

TABLE 2. Hydrogenated Adducts

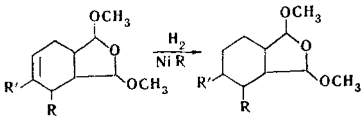
Compound	Obt. from	Bp, °C (press., mm)	n_D^{20}	d_4^{20}	MR_D		IR spectrum, ν_{OCH_3}, cm^{-1}	Empirical formula	Found, %		Calc., %		Yield, %
					Found	Calc.			C	H	C	H	
XI	III	71—75 (4)	1,4588	1,032	49,31	48,91	2835	$C_{10}H_{18}O_3$	63,82 63,56	9,83 10,07	64,49	9,74	80
XII	IV	83—87 (2,5)	1,4575	1,012	53,93	53,53	2830	$C_{11}H_{20}O_3$	65,84 65,92	10,01 10,06	65,97	10,06	75
XIII	VI	86—90 (3)	1,4620	0,994	58,58	58,15	2830	$C_{12}H_{22}O_3$	67,35 67,63	10,36 9,83	67,25	10,35	80

The reaction of I with hexachlorocyclopentadiene was accomplished under milder conditions (in absolute toluene at 130-140 deg). Crystalline product X was isolated.

Several physical constants and the analytical data for the adducts are presented in Table 1. The IR spectra of III-X (see Table 1) confirm the characteristic features of their structures. The band at 1610-1680 cm^{-1} corresponds to the valence vibration of the C=C bond, and the low-frequency value of this band relates to X. The methoxyl group is characterized by the valence vibration frequency at 2820-2840 cm^{-1}. For VIII and IX, which have the spiroacetal structure, one should note the large number of high-intensity bands from 980-1105 cm^{-1}; these are associated with the valence vibrations of the C–O–C and C–O–C–O–C bonds [4,5]. The valence vibration of the C–Cl bond in X is manifested as an intense band at 695 cm^{-1} [6].

The presence in adducts III-X of several asymmetric carbon atoms and the possibility of cis-trans isomerism relative to the tetrahydrofuran ring permit the existence of these substances in the form of a mixture of isomers; this is particularly confirmed by thin-layer chromatography.

The following products (see Table 2 for the physical constants and analytical data) were isolated from the catalytic hydrogenation of adducts III, V, and VI at room temperature under hydrogen pressure in the presence of a Raney nickel catalyst:



XI-XIII

R,R′=H XI; R=H, R′=CH$_3$ XII; R,R′=CH$_3$ XIII

IR spectrum, cm^{-1}		Empirical formula	Found, %		Calc., %		Yield, %
$\nu_{C=C}$	ν_{OCH_3}		C	H	C	H	
1660	2840	$C_{10}H_{16}O_3$	65,09 66,28	9,15 8,68	65,19	8,75	27
1675	2840	$C_{11}H_{18}O_3$	67,01 67,07	9,25 9,13	66,64	9,15	26,5
1680	2840	$C_{11}H_{18}O_3$	67,00 66,67	8,81 8,99	66,64	9,15	20
1675	2840	$C_{12}H_{20}O_3$	67,95 68,40	9,44 9,33	67,89	9,49	48
1675	2835	$C_{12}H_{20}O_3$	67,93 68,01	9,39 9,47	67,89	9,50	38
1627	2835	$C_{15}H_{24}O_3$	71,70 71,78	9,25 9,74	71,39	9,58	23
1630	2820	$C_{14}H_{20}O_3$	70,93 71,00	8,70 8,75	71,16	8,53	26
1610	2840	$C_{11}H_{10}O_3Cl_6$	32,78 32,73	2,60 2,69	32,79	2,50	20

The valence vibrational frequency of the C=C bond at 1620-1680 cm^{-1} is absent in the IR spectra of XI-XIII.

EXPERIMENTAL

Compounds I and II were obtained by the methods described in [5,7].

Diene Synthesis of iso-(4,7,8,9-Tetrahydro)benzo-1,3-dimethoxy-tetrahydrofuran (III). A mixture of 39 g (0.3 mole) of I, 32.4 g (0.6 mole) of previously condensed butadiene, and a small amount of hydroquinone was heated at 200 deg for 13-15 h in a 150-ml autoclave. The contents of the autoclave were then vacuum distilled to give 15 g (27%) of product.

4-Methyl- (IV), 5-methyl- (V), 4, 5-dimethyl- (VI), and 4,7-dimethyl-iso-(4,7,8,9-tetrahydro)benzo-1,3-dimethoxytetrahydrofuran (VII), spiro[4,5-dimethyl-iso-(4,7,8,9-tetrahydro)benzo-1-methoxytetrahydrofuran-3,3'-(1'-methyltetrahydrofuran)] (VIII), and spiro{bicyclo[2.2.1]-5-heptene-1-methoxytetrahydrofuran-3,3'-(1'-methyltetrahydrofuran)} (IX) were similarly obtained.

1,4,5,6,7,7,-Hexachlorobicyclo[2.2.1]-5-heptane-2,3-(α, α'-dimethoxy)tetrahydrofuran (X). Compound I [6.5 g (0.05 mole)], 8 ml (0.05 mole) of hexachlorocyclopentadiene, and 20 ml of absolute toluene were placed in a 50-ml round-bottomed flask equipped with an air condenser. The flask was heated on a glycerin bath for 10 h at 130-140 deg. After removal of the toluene and unchanged starting materials at reduced pressure, the residue in the flask began to crystallize. The adduct crystals were purified by five crystallizations from ethanol to give 20% of a product with mp 161-162 deg.

Hydrogenation. The typical experimental method was as follows. A mixture of 0.12 mole of the adduct, 100 ml of anhydrous alcohol, and 4 g of Raney nickel was hydrogenated in a rotating autoclave at room temperature with an initial hydrogen pressure of 100 atm. After the calculated amount of hydrogen had been absorbed, the hydrogenate was removed from the autoclave and freed of catalyst. The solvent was removed under reduced pressure, and the residue was vacuum distilled.

Isohexahydrobenzo-1,3-dimethoxythtrahydrofuran (XI), 5 methyl- (XII), and 4,5-dimethylisohexahydrobenzo-1,3-dimethoxytetrahydrofuran (XIII) were obtained via this route.

Chromatography and IR Spectra. The chromatographic analysis was carried out in a loose, thin layer of activity II aluminum oxide. The mobile phase was hexane–ethyl acetate (19 : 1). The compounds were applied in ethanol solutions. The developer was iodine.

The IR spectra were recorded with a UR-10 double-beam spectrophotometer from 700-3200 cm^{-1}. The liquid substances were investigated in a capillary-thin layer between potassium bromide plates, while crystals were studied in the form of mineral oil pastes.

LITERATURE CITED

1. N. O. Brace, J. Am. Chem. Soc., 77, 4157 (1955).
2. K. Alder, H. Betzing, and K. Heimbach, Ann., 638, Nos. 1-3, 187 (1960).
3. A. A. Ponomarev, I. A. Markushina, G. E. Marinicheva, USSR Author's Certificate No. 253,806; Byull. Izobr., No. 31, 30 (1969).
4. R. N. Jones, E. Katzenellenbogen, and K. Dobriner, J. Am. Chem. Soc., 75, 158 (1953).
5. A. A. Ponomarev and I. A. Markushina, Zh. Obshch. Khim., 31, 554 (1961).
6. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
7. A. A. Ponomarev and I. A. Markushina, Zh. Obshch. Khim., 30, 976 (1960).
8. A. D. Peshekhonova and T. N. Shcherbakova, Khim. Geterotsikl. Soedin., 1587 (1970).