ethyl ketone was refluxed for 20 h. It was then cooled, and the resulting precipitate was removed by filtration and washed with ether. The combined filtrate was treated with 10% alkali solution, and the organic layer was separated and dried over K_2CO_3. The ether and methyl ethyl ketone were removed by distillation, and the product was isolated by fractionation in vacuo (Table 1).

Compounds IIb-e were similarly obtained.

4-Methyl-5-(o-hydroxyphenyl)-5,6-dihydropyran (IIIa). A 4.75-g (25 mmoles) sample of IIa was heated in 30 ml of N,N-dimethylaniline to 170°C and maintained at this temperature for 4 h. The mixture was then cooled and subjected to fractional distillation *in vacuo*, as a result of which, dimethylaniline and product IIIa were isolated.

Compounds IIIb-e were similarly obtained (Table 1).

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REACTIONS INVOLVING SHIFTING OF THE DOUBLE BOND IN CYCLIC ETHERS

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4-Methylenetetrahydropyran undergoes isomerization to 4-methyl-5,6-dihydropyran in the presence of sodium on aluminum oxide. Both pyrans are converted to a vinyl ether, viz., 4-methyl-2,3-dihydropyran, under the influence of iron pentacarbonyl.

The isomerization of olefins with shifting of the double bond is a rather widespread reaction that is often used in synthetic organic chemistry. However, there are not many examples of this sort in the six-membered cyclic ether series. In the present research we examined the known reactions involving shifting of the double bond as applied to some dihydro- and 4-methylenetetrahydropyrans.

The conversion of 4-methyl-5,6-dihydropyran (I), when it is passed over CaO at 250-350°C, is very slight, and the expected vinyl ether, viz., 4-methyl-2,3-dihydropyran (II), is formed in trace amounts. The conversion of dihydropyran I increases when the temperature is raised (450-500°C), but this is due mainly to thermal cracking to give isoprene and formaldehyde.

Examples of the successful use of potassium tert-butoxide as a catalyst for the isomerization of dihydrofurans [1] and 2-alkyl-5,6-dihydropyrans [2] are known. However, the reaction of this alkoxide with dihydropyran I and 4-methylenetetrahydropryan (III) under conditions close to those described in [2] was accompanied by pronounced resinification, and the yield of II in both cases did not exceed 3%, although a high degree of conversion of the ethers (72-100%) was achieved. The introduction of dimethyl sulfoxide (DMSO), which usually promotes shifting of the double bond as a consequence of an increase in the basicity of the catalyst, also did not give the desired results. Judging from the data in [2], the presence of 2R-substituents, upon the whole, promotes isomerization; the formation of both 3,6- and

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TABLE 1. Isomerization of Tetrahydropyran III on Na/Al_2O_3

No.	Na:III ratio, mole	III concn., %	Reaction time, h	Temp., °C	III concn., %	Yield of II, %
1	1:2,8	100	1	60	—	—
2	2:1	26	3	60	28	36
3	2,2:1	22	2	80	71	16
4	2,5:1	21	2	80	88	6
5	2,8:1	20	2	60	17	55
6	2,7:1	20	4	60	68	38
7	4,9:1	17	2	60	86	30
8	4,4:1	11	2	60	61	50
9	8,4:1	11	2	60	100	—
10	4,1:1	7	2	60	25	52

TABLE 2. Isomerization of I and III in the Presence of $Fe(CO)_5$

Starting substance	Reaction time, h	Conversion, %	Yield, %	
			II	I
I	5	54	59	—
I	10	71	65	—
III	5	44	49	37
III	10	75	75	25

2,3-dihydropyrans is possible in this case. The latter is excluded in the absence of a hydrogen atom in the 2 position of the ring, as, for example, in isomeric 1-oxa-4-methylspiro-[5.5]3- and -4-undecenes (IV, V) and 1-oxa-4-methylenespiro[5.5]-undecane (VI). Heating a mixture of IV-VI in the presence of potassium tert-butoxide is accompanied primarily by conversion of IV and VI to undecene V (its percentage in the reaction mixture increases from 38% to 52%), and the yield of the corresponding vinyl ether VII amounts to $\sim$3%. It is interesting to note that VI undergoes partial isomerization (1%) with a change in the ring size to give 2-(1-cyclohexenyl)-3-methyltetrahydrofuran (VIII).

The terminal double bond in olefins is shifted effectively under the influence of catalytic amounts of finely dispersed sodium applied to Al_2O_3 [3]. However, for the isomerization of tetrahydropyran III to I no less than a twofold (with respect to the ether) excess of the reagent was required, whereas dihydropyran I was not converted to isomer II even under these conditions. By varying the reaction conditions (the Na:ether ratio, the III concentration, the temperature, and the reaction time), we were able to bring the yield of dihydropryan I up to 52-55% (Table 1). However, as a rule, the selectivity decreases as the degree of conversion of the olefin increases; this is evidentally associated with resinification on the catalyst surface. It should be noted that the isomerization of III to II (30% yield) was previously realized [4] in the gas phase at 270°C over quartzite in the presence of water vapor.

The most effective system for the synthesis of the vinyl ether proved to be $Fe(CO)_5$–NaOH. Judging from the patent data [5], dihydropyran II is formed from isomer I with a selectivity of up to 90%. However, the experiments that we carried out under similar conditions for 5 and 10 h led to more modest results, viz., 59% and 65% (Table 2). One might have expected that in the case of III the principal product, at least for a moderate degree of conversion, would be dihydropyran I. However, in conformity with the data obtained (Table 2), the formation of the vinyl ether prevails, and I is obtained only along with it.

EXPERIMENTAL

Analysis of the reaction products was carried out by chromatography with an LKhM-8MD (flame-ionization detector, 3000 by 3 mm, 20% PEGA on Celite-545, He 30-35 ml/min, 110°C, cumene internal standard); in the case of a mixture of IV-VI analysis was carried out by chromatographic mass spectrometry with a Finnigan-4021 spectrometer (30 m by 0.25 mm, glass, SE-30, He 1 ml/min, 5°C/min from 50°C to 180°C; 70 eV, one spectrum per second, 250°C).

1. Isomerization of I and III in the Presence of CaO. The reaction was carried out in a quartz tube filled with the catalyst and placed in an electric furnace with a stream of nitrogen flowing through the system. The feed rate of I was regulated by a controlled-volume

pump and was maintained at 0.1 ml/min. The nitrogen flow rate was 45 ml/min. The reaction products were collected in a receiver (cooled with ice) and analyzed.

2. Isomerization in the Presence of Potassium tert-Butoxide. This was accomplished at 180-210°C in an autoclave by the method in [1]. Mass spectrum (m/z, relative intensity, %): VII: 41 (20),* 43 (34.8), 55 (9.9), 67 (11.0), 95 (34.9), 109 (11.6), 123 (100.0), 166 (12.0); VIII: 41 (51.3), 43 (13.0), 53 (20.0), 54 (19.0), 55 (36.7), 67 (46.0), 68 (26.5), 71 (100.0), 79 (15.3), 81 (90.4), 84 (14.1), 95 (26.1), 96 (86.6), 97 (8.9), 166 (17.6).

3. Isomerization on Na/Al_2O_3. The catalyst was prepared by the method in [3], a solution of I or III in dry heptane was added, the mixture was thermostatted, and the reaction was carried out with stirring. After cooling, the reaction mixture was analyzed (Table 1).

4. Isomerization under the Influence of Iron Pentacarbonyl. A mixture of 9.8 g (0.1 mole) of I or III, 0.2 g of powdered NaOH, and 0.2 g of $Fe(CO)_5$ was placed in an autoclave and the mixture was heated at 180°C as argon was blown through it. The precipitate that formed after the reaction mass was cooled was removed by filtration, and the solution was washed with water, dried with $MgSO_4$, and analyzed (Table 2).

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*The fragments with intensities ⩾10% with respect to the maximum peak are presented.

PHOTOLYSIS OF 5-DIAZO-2,2-DIMETHYL-4,6-DIOXO-1,3-DIOXANE (DIAZOISOPROPYLIDENEMALONIC ACID)†

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The principal pathway in the photochemical (λ > 210 nm) transformation of 5-diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxane in an aqueous medium (or in methanol) is splitting out of nitrogen and the Wolff rearrangement to give the stable 2,2-dimethyl-5-oxo-1,3-dioxolane-4-carboxylic acid (or its methyl ester), which undergoes decarboxylation only at temperatures above 150°C, whereas it undergoes hydrolysis to a hydroxymalonic acid in the presence of trifluoroacetic acid.

One of the most characteristic reactions of 2-diazo ketones is the Wolff rearrangement [2]. For a long time it was supposed that a similar intramolecular process, viz., [1, 2] migration of an alkoxy group to an electrophilic center, is not realized in the diazo ester series [3]. However, it was subsequently established, both in the photolysis and in the thermolysis of various acyclic esters of diazoacetic and diazomalonic esters (see, e.g. [4, 5]), that products of the Wolff rearrangement are formed (in low yields). The question of the Wolff rearrangement of a cyclic ester of diazomalonic acid, viz., 5-diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxane (I), remained a subject of dispute.

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†Communication 6 from the series "Chemistry of diazo dicarbonyl compounds." See [1] for Communication 5.

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