We should note that randomness arises only upon rapid stirring of the solution. We attribute this phenomenon to the participation of oxygen in the autocatalytic oxidation of MA initiated by the reaction of O_2 with $\dot{C}H(CO_2H)_2$ radicals.

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NITROMETHANE–LITHIUM PERCHLORATE SYSTEM AS AN EFFECTIVE STIMULATOR FOR SKELETAL REARRANGEMENTS IN Ad_E REACTIONS OF SULFUR-CONTAINING REAGENTS

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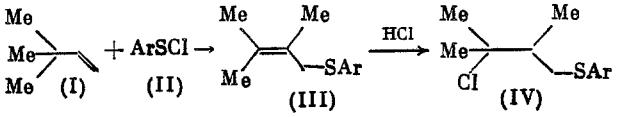
Molecular rearrangements do not occur in the reactions of tert-butylethylene (I) with sulfene halides, for example, with such typical representatives of this group of electrophiles as 2,4-dinitrophenyl chloride (II) either under "doping addition" conditions [1] or upon the usual quenching of the corresponding episulfonium ions by nucleophile-active compounds [2].

We have found that the reaction of (I) with (II) in the CH_3NO_2–$LiClO_4$ system predominantly features skeletal rearrangement with the formation of 2,3-dimethyl-4-(2,4-dinitrophenylthio)-2-butene (III) and 2,3-dimethyl-1-(2,4-dinitrophenylthio)-3-chlorobutane (IV) (~80% as indicated by PMR spectrum of the reaction mixtures). The usual product of 1,2-addition is also formed in ~20% yield.

The primary product of the skeletal rearrangement is unsaturated sulfide (III), which reacts with liberated HCl to form (IV), while the 1,2-addition product does not undergo any marked transformations under the reaction conditions. Hence, (III) is obtained directly in an Ad_E process.



Ar = 2,4-$(NO_2)_2C_7H_3$.

The formation of the products of a 1,2-methyl shift in the reaction of (I) with (II) in the $LiClO_4$–CH_3NO_2 system indicates the intermediate formation of a cationoid intermediate such as an episulfonium ion under these conditions. This should be compared with the data for the 1,2-methyl shift in S-aryl-tert-butylepisulfonium tetrafluoroborates [2].

The product structures were demonstrated by elemental analysis, meass spectrometry, and PMR spectroscopy.

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EFFECT OF PHASE TRANSITION OF THE SOLVENT ON SELECTIVITY IN HIGH-PRESSURE GLYCOSYLATION

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In previous work [1], we found a significant increase in the stereoselectivity in high-pressure glycosylation, reaching virtually absolute steric specificity at 1400 MPa [1].

The major increase in stereoselectivity in the glycosylation reaction between 1,2-O-exocyanoethylidene-3,4,6-tri-O-acetyl-α-D-glucopyranose (I) and β-O-methyl-2,4,6-tri-O-acetyl-3-O-trityl-D-glucopyranoside (II) catalyzed by $TrClO_4$ (III) occurs at 1400 MPa after crystallization of the solvent (Table 1). The phase transition of pure CH_2Cl_2 (P = 1250 MPa at 20°C) and the reaction mixture (P = 1400 MPa at 20°C) was detected relative to a sharp pressure drop by 51-52 MPa, which occurs as a result of a volume decrease upon the crystallization of CH_2Cl_2.

The β/α ratio increases by a factor of 4 with increasing pressure up to 1300 MPa, while this ratio increases by a further factor of 5 upon a subsequent increase in pressure of only 60 MPa. The glycosylation, which proceeds entirely nonstereospecifically under ordinary conditions, gives 95% β-isomer at 1400 MPa in combination with the solvent phase transition and the yield of the isomers increases to 70%.

TABLE 1. Steric Selectivity in Glycosylation at Different Pressures for 0.2 mmole (I), 0.2 mmole (II), and 0.0145 mmole (III) in 2.3 ml CH_2Cl_2 at 20°C over 4 h

P, MPa	0,1	200	400	600	800	1000	1200	1300	1360
β-Isomer, %	5,3	8,9	–	15,0	23,0	30,6	36,4	40,8	65,0
α-Isomer, %	5,9	6,9	–	7,0	8,5	10,2	10,9	11,5	3,5
β/α	0,92	1,3	1,6	2,1	2,7	3,0	3,3	3,5	19

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