Reagent (IIIc) which we were the first to obtain (mp 108°C) reacts with RI to form alkyl triflates ROTf ($R = C_6H_{13}$, 4 h, 45%; $R = CH_2CO_2CH_3$, 50 h, 45%).

Thus, the reaction of alkyl iodides with aryliodoso derivatives (I)-(III) proceeds with substitution of the iodine atom in the alkyl iodide by a weakly nucleophilic group. This reaction expands the range for the application of aryliodoso derivatives in organic synthesis.

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MASS SPECTROMETRIC DETECTION OF ALLYLIC AND PERFLUOROALLYLIC FREE RADICALS AND THE DETERMINATION OF THEIR IONIZATION POTENTIALS

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In a direct mass spectrometric study of the intermediates of a series of gas-phase thermal reactions, we detected allylic (I) and perfluoroallylic (II) free radicals and determined the previously unknown ionization potential (IP) of (II).

Radicals (I) and (II) were obtained in the thermal dissociation of 1,5-hexadiene (III), allyl bromide (IV), and 1,5-perfluorohexadiene (V) in a quartz or ceramic vacuum pyrolysis system (35 × 0.5 mm) at 600-1000°C and 0.01 torr. The pyrolysis system was directly connected to the ionization chamber of an MKh 7301/7303 [1] or MS-902 mass spectrometer [2]. Radical (I) was detected by the sharp increase in the relative intensity of the $C_3H_5^+$ ion in the mass spectra of the products of the pyrolysis of (III) and (IV) at 850°C. Above 950°C, the formation of allene, propylene, and benzene from (III) was noted as well as a decrease in the yield of (I) in accord with the results of a study of this reaction using matrix IR spectroscopy [4]. The measured ionization potential of (I) (8.18 ± 0.07 eV) is in accord with the value given by Lossing [3] (8.16 eV), which demonstrates the suitability of this technique [5].

The generation of (II) from (V) is indicated by the increase in the $I_{C_3F_5^+}/I_{C_6F_{10}^+}$ or $I_{C_3F_5^+}/I_{C_3F_7^+}$ intensity ratio with an increase in the temperature of the pyrolysis of (V) to 950°C. The ionization curves obtained up to 12 eV at different temperatures (in comparison with benzene) permitted determination of the ionization potential of (II) (8.44 ± 0.05 eV). The similarity in the ionization potentials of (I) and (II) indicates a similar type of removal of the unpaired electron upon ionization from the nonbonding π-orbitals which have similar energies in contrast to the HOMO of propylene with 9.73 eV ionization potential and of perfluoropropylene with 11.11 eV ionization potential [6]. The value found for

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the ionization potential of (II) permits the reliable demonstration of the presence of (II) in various reaction systems.

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C-ADDITION OF DIMETHYL PHOSPHITE TO p-BENZOQUINONE

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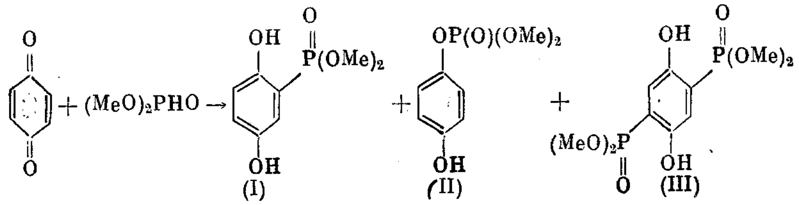
It is well known that in contrast to aldehydes and ketones which, in the presence of basic catalysts, add dialkyl phosphites at the carbonyl group carbon atom, p-benzoquinone under these conditions gave the products of O–P addition, namely, dialkyl-p-hydroxyphenyl phosphates. We have discovered that in the absence of base, dimethyl phosphite adds mainly at the terminal carbon atom of p-benzoquinone and a C-phosphorylated hydroquinone (I) is formed in 55% yield. Isomeric dimethyl-p-hydroxyphenyl phosphate (~10% yield relative to the ^{31}P NMR spectral data, δ 5 ppm) and hydroquinone (III) (8% yield) which is C,C-diphosphorylated in the ring, are also found

(III)



Maintenance of a solution of p-benzoquinone in a fivefold molar excess of dimethyl phosphite at 20°C for three weeks leads to the complete disappearance of quinone, as indicated by thin layer chromatography. The excess phosphite was removed in vacuum and tetramethyl-2,5-dihydroxy-1,4-phenylene diphosphonate (III) was crystallized at 0°C over 3 h from the residue as colorless needles with mp 126°C (reprecipitated from ether by high-boiling petroleum ether), $\delta^{31}P$ 24 ppm. PMR spectrum (CCl_4, δ, ppm): 3.70 m ($4CH_3$), 6.97 t ($J_{HP_a} + J_{HP_b} = 7$ Hz, 2H in Ar), 11.56 s (2HO). IR spectrum (vaseline suspension, ν, cm^{-1}): 1210 (P=O), 1270 (POC) UV spectrum (methanol, λ_{max}, nm(ε_{max})): 220.5 (11,000), 337 (6500). Dimethyl-2,5-dihydroxyphenyl phosphonate (I) slowly crystallized from the filtrate at 0° as colorless needles with mp 136.5°C (from benzene), $\delta^{31}P$ 22 ppm. PMR spectrum ($(Me_2N)_3PO$, δ, ppm): 3.70 m ($2CH_3$, $J_{HP} = 11$ Hz), 7 m (3H in Ar), 9.86 s and 10.67 s (···H–OAr + ···HOAr). IR spectrum (vaseline suspension, ν, cm^{-1}): 1210 (P=O), 1275 (POC), 3000-3500 (···H–OAr).

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