CONVENIENT METHOD FOR THE SELECTIVE OXIDATION OF SULFIDE SULFUR IN ALKYLMERCAPTOALKYL ESTERS OF THIO- AND DITHIOACIDS OF PHOSPHORUS

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One of the most difficult problems in studies of the metabolism of alkylmercaproalkyl esters of thio- and dithioacids of phosphorus is the synthesis of metabolites oxidized at the sulfide sulfur, i.e., the sulfoxides and sulfones

$$R(C_2H_5O)P(X)S(CH_2)_mS(O)_nR' \quad (I)$$

where X = S or O, and m and n = 1 or 2.

There is no general method for the synthesis of compounds of this type, although some representatives have been obtained by different methods. Thus, O,O-diethyl-S-(2-ethylmercaptoethyl)dithiophosphate (M-74) was oxidized with 30% and 80% H_2O_2 to the sulfoxide (Ia) (R = C_2H_5O, R- = C_2H_5, X = S, m = 2, n = 1) and the sulfone (Ib) (R = C_2H_5O, R' = C_2H_5, X = S, m = 2, n = 2) [1, 2], respectively. The same compounds have also been prepared by reacting ethyl vinyl sulfoxide and sulfone with diethyldithiophosphoric acid [1-3], or ethyl 2-chloroethyl sulfoxide with potassium diethyldithiophosphate [2].

O,O-Diethyl-S-(ethylmercaptomethyl)dithiophosphate (thimet) has been oxidized with perbenzoic acid [1] to the corresponding sulfoxide (Ic) (R = C_2H_5O, R' = C_2H_5, X = S, m = 1, n = 1) and sulfone (Id) (R = C_2H_5O, R' = C_2H_5, X = S, m = 1, n = 2), although the latter compound was not obtained in the pure state. The yields of oxidation products are in general low. 3-Chloroperbenzoic acid, $KMnO_4$, and $NaIO_4$ have also been used to oxidize analogs of thimet and their monothio derivatives [4].

The present investigation included the development of a convenient method for the synthesis of metabolites of O-ethyl-S-(methoxycarbonylmethylmercaptomethyl)methyldithiophosphonate (Ie) (R = CH_3, R' = CH_2COOCH_3, X = S, m = 1, n = 0) oxidatively activated at the sulfide sulfur, the corresponding monothiophosphonate (the same, but with X = O) (If), and some other compounds with sulfide S atoms, together with metabolites of the hydrolytic detoxification of (Ie) [O-ethyl-S-(carboxymethylmercaptomethyl)methyldithiophosphonate (Ig), R = CH_3, R' = CH_2COOH, X = S, m = 1, n = 0], which were required for the study of the metabolism of the insectoacaricides (Ie) and (If) [5, 6].

Two routes for the synthesis of O-ethyl-S-(carboxymethylsulfinylmethyl)methyldithiophosphonate (Ih) (R = CH_3, R' = CH_2COOCH_3, X = S, m = 1, n = 1) and its monothio analog (the same, but X = O) (Ii)], were developed

$$[CH_3(C_2H_5O)PXS]^-M^+ + \underset{(II)}{BrCH_2S(O)CH_2COOCH_3} \rightarrow CH_3(C_2H_5O)P(X)SCH_2S(O)CH_2COOCH_3 + MBr \quad (A)$$

$$CH_3(C_2H_5O)P(X)SCH_2SCH_2COOCH_3 \xrightarrow{[O]} CH_3(C_2H_5O)P(X)SCH_2S(O)CH_2COOCH_3 \quad (B)$$

where X = S or O, and M = K or Na.

When route A was used, the required starting material was bromomethyl methoxycarbonylmethyl sulfoxide (II)

$$\underset{(III)}{BrCH_2SCH_2COOCH_3} \xrightarrow{[O]} \underset{(II)}{BrCH_2S(O)CH_2COOCH_3}$$

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In the synthesis of this compound by the oxidation of bromomethyl methoxycarbonylmethyl sulfide (III),* due regard must be paid to the ease of cleavage of the halomethyl groups, and the hydrolytic instability of the methoxycarbonyl group and the bromine, in particular [8].

In developing the oxidative method, we initially used the much more stable chloromethyl methoxycarbonylmethyl sulfide (IV).† It was found that it was oxidized under mild conditions in about 70% yields to chloromethyl methoxycarbonylmethyl sulfoxide (VI) on treatment with 1 mole of H_2O_2 in anhydrous t-butanol in the presence of catalytic amounts of V_2O_5 [9, 10]. The bromomethyl sulfoxide (II) was obtained similarly, and this on reaction with potassium O-ethyl methyldithiophosphonate gave (Ih) in high yields.‡

Since this method of oxidation gave good results with the extremely labile halomethyl sulfides, it was employed using the same conditions for the direct conversion of the sulfide (If) into O-ethyl-S-(methoxycarbonylmethylsulfinylmethyl) methyldithiophosphonate (Ii) (R = CH_3, R' = CH_2COOCH_3, X = O, m = 1, n = 1) (method B). The latter was obtained in 50% yield.

We subsequently used this method to prepare the corresponding dithiophosphonate (Ih). For this purpose, we first checked the stability of the thione sulfur atom to oxidation under these conditions, using the model compounds O,O,O-triethyl thiophosphate and O,O,S-triethyldithiophosphate. It was found that the P = S group was oxidized only under much more severe conditions (about 80°C). This made it possible to oxidize the sulfide (Ie) to the sulfoxide (Ih) in 71% yield. The constants of the compound thus obtained and that obtained by route A were in good agreement. In order to establish the general applicability of this method of oxidation, it was extended to the preparation of the previously described [1-3] sulfoxides of the compounds M-74 (Ia) and thimet (Ic), which were obtained in 80-85% yields. The use of two moles of the oxidant was examined in order to prepare the sulfones, and it was found that the sulfoxides were further oxidized to the sulfones at 40°C. In this way, the sulfones of M-74 and thimet (Ib and Id)** were obtained in approximately 45% yields. Simultaneously, 10-40% of the corresponding sulfoxides, readily separable from the sulfones, were also formed. Attempts to carry out the oxidation with a large excess of H_2O_2 resulted in degradation of the products.

The structures of the compounds obtained were established by IR and NMR spectroscopy. The constants, yields, and elemental analyses are given in Table 1 and in the experimental section. The hydrolytic detoxification metabolite of (Ie), acid (Ig), was obtained by reacting disodium mercaptoacetate with O-ethyl-S-chloromethyl methyldithiophosphonate [12] (Table 1)

$$CH_3(C_2H_5O)P(S)SCH_2Cl + NaSCH_2COONa \rightarrow$$
$$\rightarrow CH_3(C_2H_5O)P(S)SCH_2SCH_2COONa \xrightarrow{HCl}$$
$$\rightarrow CH_3(C_2H_5O)P(S)SCH_2SCH_2COOH$$

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrophotometer. PMR spectra were recorded on a Perkin-Elmer R-12 (60 MHz), external standard HMDS, and $^{31}P-\{^1H\}$ spectra on a Bruker HX-90 (36.43 MHz), external standard 85% H_3PO_4.

5-7% H_2O_2 in anhydrous tert-butanol was prepared as in [10], the concentration being determined by iodometry. The products were purified by chromatography on a 35 × 200 mm column

*The bromomethyl sulfide (II) was obtained similarly to the chloromethyl derivative [7].
†It should be noted that the method recommended for the oxidation of chloromethyl sulfides to sulfoxides by reaction with SO_2Cl_2 in the presence of moist SiO_2 [8] resulted only in the chlorination of (IV) to chloromethyl methoxycarbonylchloromethyl sulfide (V).
‡The chloromethyl sulfoxide (VI) reacts poorly with O-ethyl methyldithiophosphonate as a result of the lower reactivity of the chlorine atom in comparison with the chloromethyl sulfide (IV) [11].
**In an attempt to oxidize (Ie) to the sulfone, the second mole of oxidant was consumed only in degrading the sulfoxide (Ih) formed.

TABLE 1. Constants and Analyses for Compounds $R(C_2H_5O)P(X)SCH_2Y$

Compound	R	X	Y	Yield, %	n_D^{20}	d_4^{20}	*MR* found	*MR* calculated	Found/Calculated, % C	Found/Calculated, % H	Found/Calculated, % P	Molecular formula
(Ia)	C_2H_5O	S	$CH_2S(O)C_2H_5$	85	1,5416[a]	1,2156	75,18	75,08	32,89 / 33,08	6,44 / 6,60	10,77 / 10,66	$C_8H_{19}O_3PS_3$
(Ib)	The same	S	$CH_2SO_2C_2H_5$	43	1,5273[b]	–	–	–	–	–	10,13 / 10,11	$C_8H_{19}O_4PS_3$
(Ic)	»	S	$S(O)C_2H_5$	82	1,5443[c]	1,2365	70,59	70,46	30,38 / 30,42	5,92 / 6,20	11,10 / 11,20	$C_7H_{17}O_3PS_3$
(Id)	»	S	$SO_2C_2H_5$	45	1,5285[d]	–	–	–	29,04 / 28,75	5,71 / 5,86	10,46 / 10,59	$C_7H_{17}O_4PS_3$
(Ih)	CH_3	S	$S(O)CH_2COOCH_3$[e]	71	1,5662	1,3259	71,45	70,98	29,10 / 28,95	5,15 / 5,20	10,60 / 10,67	$C_7H_{15}O_4PS_3$
(Ii)	The same	O	$S(O)CH_2COOCH_3$	50	1,5275	–	–	–	30,72 / 30,65	5,58 / 5,51	10,90 / 11,29	$C_7H_{15}O_5PS_2$
(Ig)	»	S	SCH_2COOH	50	1,5761	1,3180	65,37	65,18	–	–	11,74 / 11,90	$C_6H_{13}O_3PS_3$

a) According to [2]: n_D^{20} 1.5390. b) According to [2], n_D^{20} 1.5220. c) According to [1], n_D^{30} 1.5365. d) According to [1], n_D^{30} 1.5251. e) Also obtained by method (A), yield 60%, n_D^{20} 1.5634, d_4^{20} 1.3283.

packed with anhydrous SiO_2 (Chemapol), 100/160μ grade, proportions by weight of carrier and compound 15:1, compound applied to the column in a 1:1 mixture with the carrier, eluent (if not otherwise specified) a mixture of hexane and acetone in concentrations varying continuously from 100:1 to 1:1, 50-70 ml fractions, separation followed by TLC on the same carrier (eluent, hexane—acetone, 4:1 and 3:2).

Bromomethyl Methoxycarbonylmethyl Sulfide (III). A stream of dry HBr gas was passed into a mixture of 8.03 g (0.26 mole) of paraformaldehyde and 18.10 g (0.17 mole) of methyl mercaptoacetate with stirring and cooling (temperature of mixture between −5°C and −10°C), until the solid had dissolved completely. Dry ether (150 ml) was added at the same temperature, and the mixture was washed with ice water (4 × 20 ml), the aqueous layer extracted with 150 ml of ether, and the extract washed with ice water (2 × 10 ml). The combined ether layers were dried over Na_2SO_4. Removal of the ether gave 19.30 g (57%) of the sulfide (III), bp 77-78°C (2 mm), n_D^{20} 1.5396, d_4^{20} 1.6223. Found: Br 40.05%; MR 37.88 $C_4H_7BrO_2S$. Calculated: Br 40.14%; MR 38.09. PMR spectrum (CCl_4, δ, ppm): 3.57 s (CH_2CO, 2H), 3.87 s (CH_3, 3H), 4.87 s (CH_2Br, 2H).

Oxidation of Alkylmercaptoalkyl Esters of Thio- and Dithioacids of Phosphorus to the Sulfoxides (Method B). V_2O_5 (0.02 g) was dissolved in 10.7-15.0 g of 0.022 mole of 5-7% H_2O_2 in tert-butanol, and after 10-15 min, when the orange-colored solution had become homogeneous, it was added in 1-3 ml portions with stirring to 0.02 mole of the alkyl-mercaptoalkyl ester of the thio- or dithioacid of phosphorus in 40 ml of anhydrous tert-butanol at 20-30°C (slight liberation of heat). Each successive portion of the oxidant was added as the solution became colorless. When all the oxidant had been added, the colorless or greenish solution was evaporated under reduced pressure, the residue dissolved in 50-70 ml of $CHCl_3$, washed with ice water (3-4 × 10 ml), dried over Na_2SO_4, and, after removal of the solvent under reduced pressure, the residue was purified by column chromatography. The eluent was removed under reduced pressure, and the product kept for 1 h at 65-70°C (1 mm). Compounds (Ia,c,h, and i) were obtained similarly (see Table 1).

(Ia). IR spectrum (ν, cm^{-1}): 655 (P=S), 1020 (POC), 1030 (S=O).

(Ic). PMR spectrum ($CHCl_3$, δ, ppm): 1.65 t (CH_3CH_2, 9H), 3.09 m (CH_2SO, 2H), 4.51 m ($\underline{CH_2}CH_3$, 6H). IR spectrum (ν, cm^{-1}): 670 (P=S), 1020 (POC), 1040 (S=O).

(Ih). PMR spectrum ($CHCl_3$, δ, ppm, J, Hz): 1.31 t ($\underline{CH_3}CH_2$, 3H), 2.13 d, 2.16 d (Δδ 0.03 ppm): (CH_3P, 3H, J_{CH_3P} = 14.7), 3.73 s, 3.77 s (Δδ 0.04 ppm) (CH_3O, 3H), 4.22 m (CH_2, 6H), $^{31}P-\{^1H\}$ ($CHCl_3$, δ, ppm): 101.86 s, 103.30 s (Δδ 1.44 ppm). IR spectrum (ν, cm^{-1}): 670, (P=S), 1020 (POC), 1040 (S=O), 1740 (C=O).

(Ii). PMR spectrum ($CHCl_3$, δ, ppm, J, Hz): 1.36 t (CH_3CH_2, 3H), 1.89 d, 1.94 d (Δδ 0.05 ppm) (CH_3P, 3H, J_{CH_3P} = 16), 3.72 s (CH_3O, 3H), 4.14 m (CH_2, 6H). IR spectrum (ν, cm^{-1}): 1015 (POC), 1040 (S=O), 1235 (P=O), 1740 (C=O).

Chloromethyl Methoxycarbonylmethyl Sulfoxide (VI). Obtained similarly, from 7.73 g (0.05 mole) of chloromethyl methoxycarbonylmethyl sulfide [7] in 100 ml of tert-butanol and 30.53 g (0.05 mole) of 5.6% H_2O_2 in tert-butanol with 0.05 g of V_2O_5. Purification on a column gave 5.85 g (68%) of the sulfoxide (VI), n_D^{20} 1.5112, d_4^{20} 1.4200. Found: C 28.06; H 4.03; S 18.75%; MR 36.01. $C_4H_7ClO_3S$. Calculated: C 28.16; H 4.13; S 18.80%; MR 36.26. PMR spectrum ($CHCl_3$, δ, ppm, J, Hz): 3.73, 3.94, AB-quadruplet ($ClCH_2$, 2H, J_{AB} = 14), 3.74 s (CH_3, 3H), 4.53, 4.67, AB-quadruplet (CH_2CO, 2H, J_{AB} = 10). IR spectrum (ν, cm^{-1}): 1040 (S = O), 1750 (C = O).

Bromomethyl Methoxycarbonylmethyl Sulfoxide (II). Obtained under the same conditions, from 9.95 g (0.05 mole) of the sulfide (III). Purification on a column gave 3.30 g (31%) of (II), n_D^{20} 1.5382, d_4^{20} 1.7298. Found: S 14.96%; MR 38.90. $C_4H_7BrO_3S$. Calculated: S 14.90%; MR 39.16. PMR spectrum ($CHCl_3$, δ, ppm, J, Hz): 4.02, 4.28, AB-quadruplet ($BrCH_2$, 2H, H_{AB} = 14.7), 4.09 s (CH_3, 3H), 4.78, 4.91, AB-quadruplet (CH_2CO, 2H, J_{AB} = 11.3).

O-Ethyl-S-(methoxycarbonylmethylsulfinylmethyl) Methyldithiophosphonate (Ih) (Method A). To 1.55 g (0.008 mole) of potassium O-ethyl methyldithiophosphonate in 10 ml of dry acetone was added dropwise with stirring 1.70 g (0.0079 mole) of bromomethyl methoxycarbonylmethyl sulfoxide (II). The mixture was kept at 20°C for 3 h, then boiled for 20 min. The precipitated KBr was filtered off, the filtrate evaporated under reduced pressure, the residue dissolved in 30 ml of $CHCl_3$ and washed with ice water, saturated $NaHCO_3$ solution, and water (10 ml portions), dried over Na_2SO_4, and following removal of the solvent under reduced pressure,

purified by column chromatography to give 1.39 g (60%) of (Ih), n_D^{20} 1.5634, d_4^{20} 1.3283. Found: P 10.33%; MR 71.04. $C_7H_{15}O_4PS_3$. Calculated: P 10.67%; MR 70.98 (cf. Table 1).

Oxidation of O,O-Diethyl-S-ethylmercaptoalkyl Dithiophosphates to the Sulfones. To 0.02 mole of M-74 or thimet in 40 ml of tert-butanol was added with stirring in portions of 1-2 ml 21.5-30 g of 5-7% H_2O_2 (0.044 mole) in tert-butanol, containing 0.02 g of V_2O_5. Half of the oxidant was added under the conditions used for the sulfoxides, then the temperature was raised to 40°C and the second half of the oxidant added. The mixture was treated as for the oxidation to the sulfoxides, and the product purified by column chromatography. The sulfones thus obtained (Ib) and (Id) were viscous oils (see Table 1). In both cases, in addition to the sulfones there were formed 10-40% of the sulfoxides, which were easily separated from the sulfones (they were eluted from the column later), and could be obtained in the pure state. (Ib). IR spectrum (ν, cm^{-1}): 655 (P = S), 1020 (POC), 1140, 1320 (SO_2).

O-Ethyl-S-(methoxycarbonylmethylmercaptomethyl) Methyldithiophosphonate (Ih). To sodium ethoxide from 0.92 g (0.02 g-atom) of sodium and 20 ml of absolute alcohol was added 1.84 g (0.02 mole) of mercaptoacetic acid. The mixture was stirred until the solution became homogeneous, then 4.09 g (0.02 mole) of O-ethyl-S-chloromethyl methyldithiophosphonate [12] was added dropwise. After heating for 2 h at 65°C, the mixture was kept overnight, diluted with 50 ml of alcohol, sodium chloride filtered off, the filtrate evaporated, the residue treated with 70 ml of benzene, the solution concentrated to 20 ml, and anhydrous ether added until all the salt had been precipitated. The hygroscopic solid was filtered off, and washed thoroughly in the filter with ether. It was then dissolved in 30 ml of dry acetone, and a solution of 0.76 g (0.02 mole) of gaseous HCl in 20 ml of acetone was added dropwise with stirring. The precipitated NaCl was filtered off, the filtrate evaporated under reduced pressure, and the residue purified by column chromatography. Eluents: $CHCl_3$ (300 ml), mixtures of $CHCl_3$ and ethyl acetate, 100:1 (100 ml), 95:5 (200 ml), and 90:10 (300 ml) (see Table 1). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 1.31 t (CH_3CH_2, 3H), 2.13 d (CH_3P, 3H, J_{CH_3P} = 14.65), 3.44 s (CH_2CO, 2H), 4.00 m (CH_2O, 2H), 4.20 d (CH_2, 2H, J_{PSCH_2} = 15.25), 9.88 s (COOH, 1H).

Chloromethyl Methoxycarbonylchloromethyl Sulfide (V). To a mixture of 7.73 g (0.05 mole) of chloromethyl methoxycarbonylmethyl sulfide, 3.75 g of SiO_2, and 3.75 ml of water in 36 ml of CH_2Cl_2 was added dropwise with stirring 7.01 g (0.052 mole) of SO_2Cl_2 in 36 ml of CH_2Cl_2. The mixture was kept for 2 h at about 20°C and 1 h at 38-40°C, washed with water, $NaHCO_3$ solution and water, dried over K_2CO_3, and the solvent removed. The product was purified by column chromatography, to give 3.15 g (33.3%) of the sulfide (V), n_D^{20} 1.5130, d_4^{20} 1.4178. Found: C 25.10; H 3.23%; MR 40.08. $C_4H_6Cl_2O_2S$. Calculated: C 25.41; H 3.19%; MR 40.06. PMR spectrum (CCl_4, δ, ppm, J, Hz): 3.81 s (CH_3, 3H), 4.83, 4.87 AB quadruplet (CH_2, 2H, J_{AB} = 9.5), 5.56 s (CH, 1H).

CONCLUSIONS

1. A general method has been developed for the oxidation of sulfide sulfur in S-mercaptoalkyl esters of thio- and dithioacids of phosphorus to the sulfoxides and sulfones.

2. The oxidative activation metabolites of O-ethyl-S-(methoxycarbonylmethylmercaptomethyl) methyldithiophosphonate and its monothio analog, and the hydrolytic detoxification metabolite of the former, have been synthesized.

LITERATURE CITED

1. R. L. Metcalf, T. F. Fukuto, and R. B. March, J. Econ. Entomol., 50, 338 (1957).
2. M. P. Shabanova, Yu. S. Kagan, E. N. Prilezhaeva, L. V. Tsymbal, and E. Ya. Makhlina, Tr. Vsesoyuz. NII Zashch. Rastenii, No. 21, part 1, p. 114 (1964).
3. M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal, V. A. Azovskaya, and N. G. Starova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2239 (1959).
4. F. A. Wagner, US Patent No. 3,878,267; Chem. Abstr., 83, 27,553 (1975).
5. T. A. Mastryukova, Z. K. Emkuzheva, A. É. Shipov, Yu. S. Kagan, E. A. Ershova, K. N. Savchenko, S. A. Roslavtseva, N. A. Guseva, T. N. Kaluzhina, V. P. Golubeva, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 637 (1979).
6. T. A. Mastryukova, A. É. Shipov, Z. K. Emkuzheva, A. P. Brestkin, I. L. Brik, Yu. E. Mandel'shtam, A. N. Fedin, T. I. Nozhko, Z. Tilyabaev, S. A. Roslavtseva, Yu. S. Kagan, E. A. Ershova, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1131 (1980).
7. W. J. Brehm and T. Levenson, J. Am. Chem. Soc., 76, 5389 (1954).

8. M. Hojo and R. Masuda, Tetrahedron Lett., 613 (1976).
9. N. A. Milas and S. Sussman, J. Am. Chem. Soc., 58, 1302 (1936).
10. F. E. Hardy, P. R. H. Speakman, and P. Robon, J. Chem. Soc., 2334 (1969).
11. F. G. Bordwell and W. T. Brannen, Jr., J. Am. Chem. Soc., 86, 4645 (1964).
12. G. Schrader, West German Patent No. 1,099,531; Chem. Abstr., 56, 3515 (1962).

REACTION OF AROMATIC NITRO COMPOUNDS WITH TRANSITION METAL COMPLEXES

2. COMPLEXES OF PLATINUM(II) WITH AROMATIC NITRO COMPOUNDS: SYNTHESIS, PROPERTIES, SPECTRA, AND STRUCTURE

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By the method of resonance combination light scattering (RCLS) spectroscopy, we have already shown [1] that in solutions of K_2PtCl_4, $PtCl_2(DMSO)_2$, and $Pt(Ml)_2$, where Ml is 3-hydroxy-2-methyl-4-pyrone, in nitrobenzene, a coordination of the nitro group with the Pt atom takes place.

Synthesis and Catalytic Properties. Complexes of Pt(II) with aromatic nitro compounds were obtained by the reaction

$$\underset{\text{(I)}}{PtCl_2(DMSO)_2} + C_6H_4NO_2R \rightarrow \underset{\text{(II)—(IV)}}{PtCl(DMSO)(C_6H_3NO_2R)} + HCl + DMSO$$

R = H(II); *p*-Cl (III); *p*-CH_3 (IV); Yield 4-8%.

A mixture of (I) and the aromatic nitro compound taken in a molar ratio of 1:100 was heated for 5-10 min at 180-230°C; dark red solutions were obtained. When cool, excess of nitro compound was removed by distillation [complex (II)] or sublimation [complexes (III) and (IV)] at reduced pressure. The residue was extracted by ether, and the extract evaporated to dryness. The residue was dissolved in a minimal amount of absolute acetone, and the impurities were precipitated by ether. After filtration and evaporation, red rhombic [(II)] or needlelike [(III) or (IV)] crystals were obtained (Table 1).

Complexes (II)-(IV) are readily soluble in acetone, ether, benzene, alcohols, halohydrocarbons, DMFA, DMSO, or nitro compounds; in aqueous solutions they decompose. Melting points of (II) 68°C, (III) 145°C (dec), of complex (IV) 160°C (dec).

During hydrogenation of (II)-(IV) by molecular H_2 it was found that they dissociate with the formation of the corresponding aniline and a Pt-containing compound, whose stability and catalytic activity depend on the solvent. In the presence of H_2, (II)-(IV) are stable in benzene, DMFA, DMA, DMSO, but do not exhibit catalytic activity with the hydrogenation of aromatic nitro compounds. The addition of $NaBH_4$ leads to decomposition of (II)-(IV) with formation of Pt black. Compounds (II)-(IV) decompose similarly in acetone in the presence of H_2.

In solutions of nitrobenzene, p-nitrotoluene, p-chloronitrobenzene, in a H_2 atmosphere at 20-80°C, compounds (II)-(IV) are catalytically active (specific activity 1.6-2.5 mole H_2/mole Pt•min). The corresponding anilines are obtained as the reaction products. If instead of H_2, $NaBH_4$ is used, a mixture is formed consisting of N-arylhydroxylamine, azoxy and hydrazo derivatives.

Electronic and Infrared Absorption Spectra of Complexes (II)-(IV). During the study of the $PtCl_2(DMSO)_2 + C_6H_5NO_2$ system by the RCLS method [1], data were obtained showing that the

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