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SOLVENT EFFECTS IN THE CHLORINATION OF TETRAHYDROTHIOPHENS WITH N-CHLOROSUCCINIMIDE

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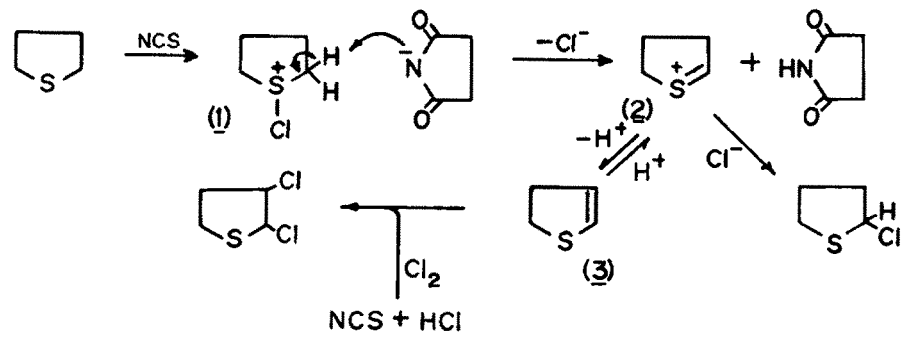
Abstract - Depending simply on solvent, the reaction of N-chlorosuccinimide with tetrahydrothiophen can be arranged to give either 2-chlorotetrahydrothiophen or 2,3-dichlorotetrahydrothiophen. In the latter case, a novel compound, 2-(4-chlorobutylthio)thiophen was isolated also. For 2-methyl- and 2,5-dimethyltetrahydrothiophen the solvent dependency was almost entirely eliminated, the principal reaction products being those resulting from dichlorination.

INTRODUCTION

Reaction of tetrahydrothiophen (THT) with chlorine[1] and sulphuryl chloride[2] has been examined extensively, and with N-chlorosuccinimide (NCS)[3] and phosphorus pentachloride[4] only briefly as parts of synthetic routes to other compounds. Reaction of 2-methylTHT and 2,5-dimethylTHT with NCS has not been reported previously.

Chlorination of THT with molecular chlorine gives mixtures of 2-chloro- and 2,3-dichloroTHT, the proportions of which are highly solvent dependent and little affected by the molar ratio of reactants. A reaction scheme to account for this pronounced solvent dependence has been advanced[1] (compare Scheme 1) and has been adapted to account for the ratio of mono- and dichlorinated products observed in the reaction of sulphuryl chloride with THT[2]. Reaction of open chain sulphides with NCS to give mono-α-chlorosulphides is thought to proceed through a mechanism involving initial formation of a chlorosulphonium salt.[5] Scheme 1 incorporates these ideas into an overall mechanism for the mono- and dichlorination of THT using NCS. Thus, initial formation of the chlorosulphonium salt (1) of THT is followed by extraction of a proton to give the sulphonium compound (2). The latter, by removal of a proton, is converted into 2-thiolene (3). Attack on



Scheme 1

compound (2) by chloride ion yields 2-chloroTHT and attack on the 2-thiolene (3) by chlorine (generated from NCS and HCl) yields 2,3-dichloroTHT. Formation of a mono- or dichloroTHT is dependent on the ratio of compounds (2, 3) and therefore on polarity and basicity of solvent.

In early experiments on the chlorination of THT, neither 2-chloroTHT nor 2,3-dichloroTHT were isolated because of their stated instability. The amounts of the two chlorination products were estimated by their reaction with methanol to give 2-methoxyTHT and 2-methoxy-3-chloroTHT respectively from the two compounds.[1,2] Subsequently, 2,3-dichloroTHT was prepared by chlorination of THT with PCl_5.[4] It is shown in the present work that reaction of THT with NCS is convenient for the preparation of either 2-chloroTHT or 2,3-dichloroTHT by simple change of solvent. These effects appear to be more pronounced than in the reaction of chlorine or sulphuryl chloride with THT. Further, product distribution was found to be somewhat dependent on the initial molar ratios of the reactants, NCS and THT, unlike the earlier chlorinations for which no dependence on the ratio of reactants was observed.

In a further investigation of these solvent effects, chlorination of 2-methylTHT and 2,5-dimethylTHT by NCS was examined.

METHOD

THT was reacted with NCS in various proportions in a variety of solvents at different temperatures. A summary of the results is shown in Table 1. As in earlier work,[1,2] the ratio of chlorination products was determined by gc of their 2-methoxy derivatives, obtained by reacting the crude reaction mixtures of 2-chloroTHT and 2,3-dichloroTHT with methanol in the presence of pyridine; the 2-chloro group is much more reactive than the 3-chloro and is rapidly substituted to give a 2-methoxy group. For 2,3-dichloroTHT, isolated yields are reported here. Chlorination product mixtures were examined further by ^{1}H-nmr and gc/ms. Similar procedures were followed for 2-methylTHT and 2,5-dimethylTHT; Tables 2 and 3 show the variations in yield of chlorination products observed with changes of solvent.

TABLE 1 Product Ratios of 2-ChloroTHT and 2,3-DichloroTHT formed from the Reaction of THT and NCS in Various Solvents.

SOLVENT	MOLAR RATIO (NCS:THT)	PRODUCT DISTRIBUTION[a]
C_6H_6	1:1	80:20
C_6H_6	1:2	90:10
C_6H_6	1:5	90:10
CCl_4	1:1	70:30
CCl_4	2:1	30:70
CCl_4	1:2	85:15
CCl_4	1:1[b]	-
CH_2Cl_2	1:1	5:95
CH_2Cl_2	2:1	2:98
$CHCl_3$	1:1	5:95

[a] Ratio of 2-chloroTHT to 2,3-dichloroTHT determined from gc measurements on the derivatives, 2-methoxyTHT and 3-chloro-2-methoxyTHT.

[b] All reactions were run at 20 - 25° for two hours except this one run at 0° when negligible chlorination was observed after two hours.

TABLE 2 Chlorination Product Ratios Observed in the Reaction of 2-MethylTHT with NCS in Various Solvents

SOLVENT	PERCENTAGE COMPOSITION OF CHLORINATED PRODUCTS[a]						
	1	2	3	4	5	6	7
CCl_4	14	10	35	31	9	0	1
C_6H_6	14	12	39	25	9	0	<1
CH_2Cl_2	7	7	36	27	14	<1	8
$CHCl_3$	8	8	32	30	16	5	<1
CH_2Cl_2[b]	8	8	36	26	6	0	16

[a] Each reaction, in which the molar ratio of 2-methylTHT to NCS was 1:1, was run for one hour before addition of methanol and pyridine to convert any 2-chloro groups to 2-methoxy (see experimental). Percentage compositions were calculated from gc/ms peak areas. Products 1,2 are the isomeric 2- and 5-methoxy-2-methylTHT; product 3 is 3-chloro-2-methyl-4,5-dihydrothiophen; products 4,5 are cis, trans-2-methyl-2-methoxy-3-chloroTHT; product 6 is 2,5-dimethoxy-2-methylTHT; product 7 is of unknown structure having a composition, $C_6H_{10}Cl_2OS$.

[b] All reactions were carried out at 20 - 25° except for this one at 0°.

TABLE 3 Chlorination Product Ratios Observed in the Reaction of 2,5-DimethylTHT with NCS in Various Solvents.

SOLVENT	PERCENTAGE COMPOSITION OF CHLORINATED PRODUCTS[a]					
	1	2	3	4	5	6
CCl_4	12	49	26	12	1	<1
C_6H_6	15	62	13	9	<1	<1
CH_2Cl_2	0	66	15	17	1	1
$CHCl_3$	0	64	11	22	2	1
CH_2Cl_2[b]	0	53	30	15	<1	<1

[a] Each reaction, in which the molar ratio of 2,5-dimethylTHT to NCS was 1:1, was run for one hour before addition of methanol and pyridine (see experimental). Percentage compositions were calculated from gc/ms peak areas. Product 1 is 2,5-dimethyl-2-methoxyTHT; product 2 is 3-chloro-2,5-dimethyl-4,5-dihydrothiophe products 3,4 are isomers of 2,5-dimethyl-2-methoxy-3-chloroTHT; product 5 is 2,5-dimethyl-2,5-dimethoxyTHT; product 6 is of unknown structure having a composition, $C_7H_{12}Cl_2OS$.

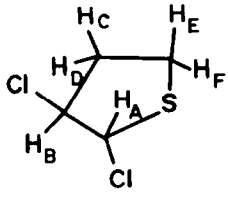
[b] All reactions were carried out at 20 - 25° except for this one at 0°.

RESULTS AND DISCUSSION

With a 1:1 ratio of NCS to THT, the more polar the solvent, the greater the amount of 2,3-dichloroTHT formed in comparison with 2-chloroTHT. Table 1 shows that, in changing from benzene to chloroform, the ratio of 2-chloroTHT to 2,3-dichloroTHT changes from 80:20 to 5:95. This degree of change in product composition has been observed for chlorination of THT with chlorine[1] and with sulphuryl chloride,[2] although not to such a pronounced extent over the same solvent range. The ratio of mono- to dichlorinated product in benzene could be increased from 80:20 to 90:10 by decreasing the molar ratio of NCS to THT to 1:2; further decrease of this ratio of 1:5 produced little effect on the product ratio. On the other hand, in the more polar solvent, methylene chloride, increasing the

ratio of NCS to THT changed the ratio of mono- to dichlorinated products to 2:98. Thus, change in the ratio of reactants had a small effect on the distribution of chlorinated product. From a practical view point, the best yield of 2-chloroTHT free from the dichlorinated material is obtained with an NCS:THT ratio of 1:2 in benzene. The best yields of 2,3-dichloroTHT are obtained at an NCS:THT ratio of 1:1 in methylene chloride. These results can be accommodated by the mechanism of Scheme 1 if the equilibrium between compounds (2, 3) is rapid and solvent dependent, as is likely for the required addition and removal of a proton.

As found by earlier workers,[1,2] 2-chloroTHT is thermally too unstable to be purified by distillation and was used without purification.[8] However, 2,3-dichloroTHT could be distilled in 55-60% yield, without serious decomposition. This difference between 2-chloro and 2,3-dichloroTHT in thermal stabilities can be attributed to the fact that the energetically and conformationally favoured trans-1,2-elimination of HCl from 2-chloroTHT is easy, but is difficult in 2,3-dichloroTHT which is formed with the two halogens arranged in a trans configuration to each other. In the 220 MHz ^{1}H-nmr spectrum of 2,3-dichloroTHT, proton H_A (Structure 4) appears as a doublet (J 1 Hz) at δ 5.62 and H_B as a triplet of doublets centred at δ 4.76.

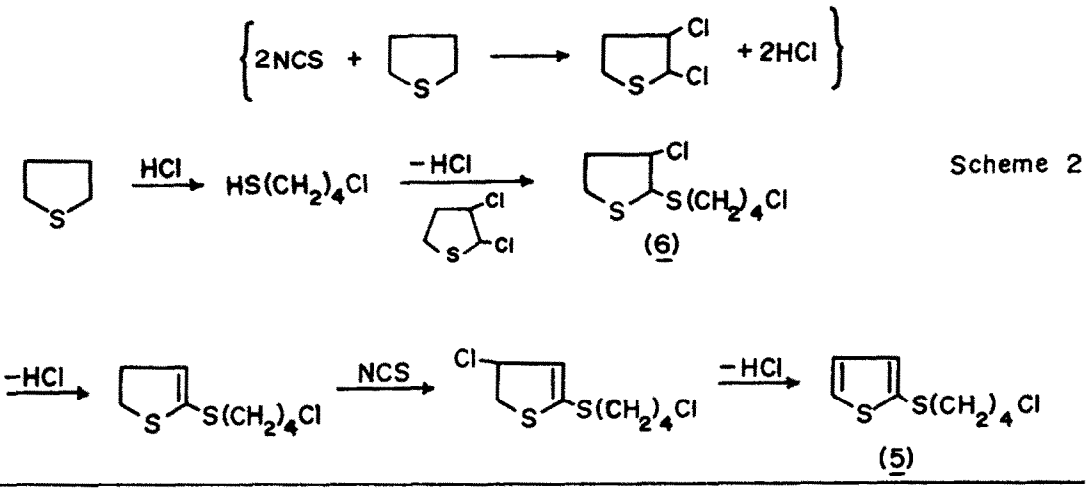


(4)

The very small vicinal coupling between H_A and H_B indicates a relative trans orientation for these two protons and hence also for the two halogens. Thus, the conformationally favoured trans-1,2-elimination of HCl from 2,3-dichloroTHT is not possible. Protons H_C, H_D appeared as multiplets at δ 2.41, 2.68 and H_E, H_F as a multiplet at δ 3.27.

The residue from the distillation of 2,3-dichloroTHT consists mainly of a previously unreported compound in which two THT residues have been coupled. This new compound was isolated as a yellow oil, the mass spectrum of which revealed the presence of one chlorine atom in the molecular ion at m/z 206, 208 and an elemental composition, $C_8H_{11}ClS_2$. The 220 MHz ^{1}H-nmr spectrum of the yellow oil showed three doublet of doublets at δ7.25, 7.09 and 6.97, indicating a 2-substituted thiophen ring. The triplet at δ3.45 was assigned to a CH_2 adjacent to Cl and the triplet at δ2.78 to a CH_2 next to S. The remaining four protons formed a multiplet centred at δ 1.75. Structure (5; Scheme 2) was deduced for this yellow oil and its possible mode of formation is shown in the Scheme. The principal steps in Scheme 2 consist of ring-opening of THT to give a chlorothiol which condenses with 2,3-dichloroTHT, the normal chlorination product. Further chlorination and thermal elimination of HCl gives the product (5), 2-(4-chlorobutylthio)thiophen. Chlorination of tetrahydrofuran has given 3-chloro-2-(4-chlorobutoxy)tetrahydrofuran,[6] an oxygen analogue of the intermediate (6; Scheme 2). Compound (5) is not formed directly from thiophen because addition of the latter to a reacting mixture of NCS and THT did not increase its yield. The isomeric 3-(4-chlorobutylthio)thiophen has been synthesized in several steps from thiophen-3-thiol.[7]

Reaction of 2-methylTHT with NCS was much faster than for THT itself. Table 2 gives the distribution of chlorinated products (1 - 7). Of these, products (3 - 6) result from dichlorination and, for methylene chloride as solvent, compose some 77% of the reaction mixture. Products (3 - 6) are 3-chloro-2-methyl-4,5-dihydrothiophen (resulting from dehydrochlorination of 2,3-dichloro-2-methylTHT) and the cis, trans isomers resulting from methoxylation of the dichloro compound. On distillation of the reaction mixture resulting from 2-methylTHT and NCS in methylene chloride, only 3-chloro-2-methyl-4,5-dihydrothiophen could be isolated, i.e., rapid dehydrochlorination occurred during distillation.



Scheme 2

Reaction of NCS with 2,5-dimethylTHT was even more vigorous than for 2-methylTHT. Table 3 gives the distribution of chlorinated products (1 - 6). Of these, products (2 - 4) result from dichlorination and, for methylene chloride or chloroform as solvent, compose some 97% of the reaction mixture. Even in benzene, only 15% of monochlorinated product is observed. Products (2 - 4) are 3-chloro-2,5-dimethyl-4,5-dihydrothiophen and the cis, trans isomers of 2,5-dimethyl-2-methoxy-3-chloroTHT. Distillation of the crude chlorination product from the action of NCS on 2,5-dimethylTHT afforded only the dehydrochlorinated product, 3-chloro-2,5-dimethyl-4,5-dihydrothiophen.

CONCLUSION

Reaction of tetrahydrothiophen with N-chlorosuccinimide is strongly influenced by the polarity of the solvent and appears to proceed via a mechanism similar to that observed in the chlorination of THT with chlorine or sulphuryl chloride. By suitable choice of solvent, either 2-chloroTHT or 2,3-dichloroTHT can be prepared in good yield. Preparation of 2,3-dichloroTHT results also in the formation of a previously unreported thiophen derivative. Reaction of N-chlorosuccinimide with either 2-methyl- or 2,5-dimethyltetrahydrothiophen leads mostly to dichlorinated products whatever the polarity of the solvent. Distillation of these last reaction mixtures gives 3-chloro-2-methyl-4,5-dihydrothiophen and 3-chloro-2,5-dimethyl-4,5-dihydrothiophen respectively.

EXPERIMENTAL

Analysis of Reaction Mixtures. Gc/ms was carried out on a VG 7070 mass spectrometer at 70 eV with helium carrier gas. Pure samples of some components, described below, were isolated by trapping them at -60° from the effluent of a gc column containing 10% Reoplex 100 on Celite and operated at about 180°. ^{1}H-n.m.r. spectra were measured in $CDCl_3$ on a Perkin-Elmer PE34 220 MHz instrument.

Conversion of Chlorination Products into Methoxy Derivatives for Analysis. To improve the stability of tetrahydrothiophens containing a 2-chloro group, and so to facilitate analysis, crude reaction products were reacted with methanol. In a typical reaction, the filtrate from reaction of N-chlorosuccinimide and tetrahydrothiophen (4g; see below for details) was treated with methanol (2g) and pyridine (5g) and the solution allowed to stand at room temperature for 18 hours. The

deposited crystals of pyridinium hydrochloride were filtered off and the filtrate was washed with dil. HCl and water and dried ($MgSO_4$). The resulting solution was evaporated to give the crude product, usually as a red oil, which was analysed by gc or gc/ms. For examination of the methoxy derivatives, by ^{1}H-nmr, pure samples were obtained by preparative gc; the purity of trapped samples was checked by analytical gc.

Typical Chlorinations of Tetrahydrothiophen. (a) To a stirred solution of tetrahydrothiophen (8.0g; 0.09 mole) in benzene (60 ml) was added N-chlorosuccinimide (6.0g; 0.045 mole) in small portions over a period of 15 minutes. Reaction temperature was maintained at 20 - 25° by cooling. After addition of all the N-chlorosuccinimide, stirring at 20 - 25° was continued for two hours after which the solution was filtered from succinimide. The yellow filtrate contained 2-chlorotetrahydrothiophen of at least 90% purity which could be used immediately for further reactions. The remaining 10% of product is trans-2,3-dichlorotetrahydrothiophen. Purity of the 2-chlorotetrahydrothiophen was confirmed by its conversion into 2-methoxytetrahydrothiophen followed by gc analysis.

(b) Preparation of 2,3-Dichlorotetrahydrothiophen. To a stirred solution of tetrahydrothiophen (16g; 0.18 mole) in methylene chloride (250 ml) was added N-chlorosuccinimide (24g; 0.18 mole) in small portions over a period of 15 min. keeping the reaction temperature at 20 - 25° by cooling. After addition of the N-chlorosuccinimide, stirring was continued for 2 hours at 20 - 25° and then the solution was filtered from succinimide. The filtrate was evaporated under reduced pressure and the residual oil was distilled to give : fraction (i), trans-2,3-dichlorotetrahydrothiophen (8.1g; 58% yield), b.p. 40 - 42°/0.13 mm; ms:m/z 160, 158, 156 [$M^{+\cdot}$; 2 Cl atoms]: fraction (ii), 2-(4-chlorobutylthio)-thiophen (5; 2.2g), b.p. 110 - 120°/0.3 mm; ms:m/z 208, 206 [$M^{+\cdot}$; 1 Cl atom]; ^{1}H-nmr ($CDCl_3$), δ 7.25 (dd, J 3,5Hz, 1H), 7.09 (dd, J 3,1.5Hz, 1H), 6.97 (dd, J 5,1.5Hz, 1H), 3.45 (t, J 6.2Hz, 2H), 2.78 (t, J 6.8Hz, 2H), 1.90 - 1.60 (m, 4H). This reaction was repeated with the further addition of thiophen (15g; 0.18 mole) to the initial reagents; the yields of 2,3-dichlorotetrahydrothiophen and 2-(4-chlorobutylthio)thiophen were unchanged.

Chlorination of 2-Methyltetrahydrothiophen. To a stirred solution of 2-methyltetrahydrothiophen (5.1g; 0.05 mole) in methylene chloride (60 ml) at 20 - 25° was added N-chlorosuccinimide (6.7g; 0.05 mole) in small portions over a period of 15 minutes. Stirring was continued for 1 hour at 20 - 25° after which succinimide was filtered off. This filtrate was worked up in one of two ways:

(a) The filtrate was evaporated under vacuum to leave an oil which was distilled to give 3-chloro-2-methyl-4,5-dihydrothiophen as a pungent, pale yellow oil (1.03g), b.p. 55 - 56°/20 mm; ms: m/z 136,134 [$M^{+\cdot}$; 1 Cl atom]; ^{1}H-nmr ($CDCl_3$); δ 3.17 (m, 2H), 2.91 (m, 2H), 1.84 (t, 3H); Found: C, 44.2; H, 5.2, C_5H_7ClS requires C, 44.6; H, 5.2%.

(b) The filtrate was reacted with an excess of methanol and pyridine as described above for the preparation of methoxy derivatives. Gc and gc/ms revealed the presence of seven components in the product mixture (Table 2). The components were identified from their mass spectra and, where indicated, by isolation of a pure specimen from the gc effluent and measurement of its ^{1}H-nmr spectrum. Components 1,2 were identified as 2-methoxy-2-methyltetrahydrothiophen and 5-methoxy-2-methyltetrahydrothiophen (ms: m/z 132 [$M^{+\cdot}$], 101 [$M-OCH_3$]$^+$); component 3 was 3-chloro-2-methyl-4,5-dihydrothiophen; components 4,5 were isomers of 3-chloro-2-methoxy-2-methylTHT (ms: m/z 168, 166 [$M^{+\cdot}$; Cl],153, 151 [$M-CH_3$]$^+$, 137, 135 [$M-OCH_3$]$^+$); components 6,7 were usually formed in only minor amounts, the first being possibly 2,5-dimethoxy-2-methyltetrahydrothiophen (ms: m/z 162 [$M^{+\cdot}$], 131 [$M-OCH_3$]$^+$, 101, 99, 88, 58, 45) and the second a dichloromethoxy compound, $C_6H_{10}Cl_2OS$ (ms: m/z 204, 202, 200 [$M^{+\cdot}$;2Cl],173,171, 169 [$M-OCH_3$]$^+$, 104, 90, 74, 59, 58, 45).

Chlorination of 2,5-Dimethyltetrahydrothiophen. To a stirred solution of 2,5-dimethyltetrahydrothiophen (5.8g; 0.05 mole) in methylene chloride (60 ml) was added N-chlorosuccinimide (6.7g; 0.05 mole) in small portions over a period of 15 minutes, the reaction temperature being maintained at 20 - 25° by cooling. Stirring was continued for 1 hour and then, after filtration from succinimide, the filtrate was worked up in one of two ways:

(a) The filtrate was evaporated under vacuum to leave an oil which was distilled to give 3-chloro-2,5-dimethyl-4,5-dihydrothiophen (1.54g), b.p. 28 - 30°/ 0.05 mm; ms: m/z 150, 148 [$M^{+\cdot}$; Cl], 135, 133 [$M-CH_3$]$^+$, 113 [M-Cl]$^+$; ^{1}H-nmr ($CDCl_3$); δ 3.74 (m, 1H), 3.10 (m, 1H), 2.56 (m, 1H), 1.88 (m, 3H), 1.38 (d, J 6.7Hz, 3H); Found: C, 48.7; H, 6.4, C_6H_9ClS requires, C, 48.5; H, 6.1%.

(b) The filtrate was reacted with an excess of methanol and pyridine as described above for the preparation of methoxy derivatives. Gc and gc/ms revealed the presence of six components in the product mixture (Table 3). The components were identified from their mass spectra and, where indicated, by isolation of a pure specimen from the gc effluent and measurement of its ^{1}H-nmr spectrum. Component 1 was 2,5-dimethyl-2-methoxytetrahydrothiophen (ms: m/z 146 [$M^{+\cdot}$], 115[$M-OCH_3$]$^+$) component 2 was 3-chloro-2,5-dimethyl-4,5-dihydrothiophen; components 3,4 were cis/trans isomers of 3-chloro-2-methoxy-2,5-dimethyltetrahydrothiophen (ms: m/z 182, 180 [$M^{+\cdot}$;Cl], 167, 165 [$M-CH_3$]$^+$, 151, 149 [$M-OCH_3$]$^+$); component 5 was possibly 2,5-dimethoxy-2,5-dimethyl-tetrahydrothiophen (ms: m/z 176 [$M^{+\cdot}$]); component 6 was a dichloromethoxy derivative, $C_7H_{12}Cl_2OS$ (ms: m/z 218, 216, 214 [$M^{+\cdot}$; 2Cl], 187, 185, 183 [$M-OCH_3$]$^+$, 118, 90, 59, 43).

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