chromatographic behavior of the products was essentially the same as in the reaction with boron trichloride.

Reaction of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-glucofuranose with Sodium Azide.—A mixture of the sulfonate ester derivative (5 g.), *N*,*N*-dimethylformamide (100 ml.), sodium azide (2 g.), water (5 ml.), and urea (1 g.) was heated for 36 hr. at 115° under a stream of nitrogen, and the reaction mixture was processed by the procedure used for 3,6-anhydro-5-azido-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose. Crystalline starting material was obtained; yield 4.5 g. (90%). When the experiment was repeated at reflux temperature, decomposition occurred during the heating period, and the recovery of starting material fell to 1.3 g. (27%). The remaining dark sirup failed to crystallize, but exhibited a weak infrared absorption at 4.8 μ, characteristic of the azido group.

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Thiono- and Thiolcarbonates

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The esterification of allyl alcohol and substituted allyl alcohols with aryl chlorothionoformates yields pure S-allyl aryl thiolcarbonates, which arise from rearrangement of the intermediate thionocarbonates accompanied by an allylic shift. The reaction between 3,4-dichlorophenyl chlorothionoformate and ethylenechlorohydrin gave S-(2-chloroethyl) 3,4-dichlorophenyl thiolcarbonate, although similar reactions with ethanol, 2,2-dichloroethanol, and, 2,2,2-trichloroethanol gave the unrearranged thionocarbonates.

The preparation of several aryl ethyl thionocarbonates has been reported,[1,2] but apparently no investigation of the biological activity of aryl alkyl thionocarbonates has been made. More interest has been shown in diaryl thionocarbonates, which may be prepared by treating phenols with thiophosgene or by treating aryl chlorothionoformates with phenols in the presence of pyridine.[3]

It was found that aryl thionocarbonates are best prepared by adding aryl chlorothionoformates to alcohols in pyridine solution at low temperatures. The procedure described by Rivier,[1,2] in which the chlorothionoformate is refluxed in ethanol, gives moderate yields with lower molecular weight alcohols. However, some of the products prepared in this way are contaminated with small amounts of the isomeric thiolcarbonates, as indicated by the presence of a weak carbonyl band at 1720–1727 cm.$^{-1}$ No rearrangement occurred in the base-promoted esterification of unsubstituted alkanols. Further, the esterification of long-chain alcohols could be achieved only in the presence of pyridine.

The new aryl chlorothionoformates are described in Table I. The aryl alkyl thionocarbonates as well as some new diaryl thionocarbonates (some of which were obtained as by-products in the preparation of the chlorothionoformates) are listed in Table II.

TABLE I

CHLOROTHIONOFORMATES ROC(S)Cl

				C		H		Cl		S	
R	Yield, %	B.p., °C./mm.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
3-Chlorophenyl	78	72/2.2[a]	$C_7H_4Cl_2OS$	40.60	40.25	1.95	2.26	34.24	34.22	15.48	15.23
4-Chlorophenyl	81	82/0.8[b]	$C_7H_4Cl_2OS$	40.60	41.00	1.95	1.93	34.24	34.21	15.48	15.66
3,4-Dichlorophenyl	83	98–100/1.3[c]	$C_7H_3Cl_3OS$	34.81	34.92	1.25	1.54	44.04	43.82	13.37	13.31
4-*t*-Butylphenyl	81	84/0.1[d]	$C_{11}H_{13}ClSO$	57.76	58.15	5.73	5.99	15.50	15.58	14.02	13.68
2-Chloro-4-nitrophenyl	50	116–118/0.25[e]	$C_7H_3C_2NO_3S$[f]	33.35	33.17	1.20	1.22	28.13	28.54	12.72	12.78

[a] $n^{25}D$ 1.59025, D^{20}_4 1.4076; [b] $n^{25}D$ 1.51273, D^{20}_4 1.4180; [c] m.p. 58–60°; [d] $n^{25}D$ 1.54901, D^{20}_4 1.4360; [e] m.p. 58–60°; [f] Calcd. N, 5.56. Found: N, 5.57.

The reaction of aryl chlorothionoformates with allyl alcohol and with substituted allyl alcohols yielded S-allyl O-aryl thiolcarbonates exclusively, as shown by the very strong C=O absorption at 1720–1727 cm.$^{-1}$. The attachment of the allyl group to the sulfur atom was established by the isolation of 2-chloro-4-nitrophenol from the hydrolysis of S-(1-methylallyl) O-(2-chloro-4-nitrophenyl) thiolcarbonate. The S-allyl derivatives were obtained by both preparative procedures. In an attempt to isolate the intermediate thionocarbonate, *p*-tolyl chlorothionoformate was treated with 2-buten-1-ol in pyridine solution at room temperature. The product, which was isolated in an analytically pure state by extraction with ether and drying at room temperature, exhibited the strong C=O absorption at 1723 cm.$^{-1}$ characteristic of thiolcarbonates.

(1) M. H. Rivier, *Bull. soc. chim. France*, (3) **35**, 837 (1906).
(2) M. H. Rivier and J. Schalch, *Helv. Chim. Acta*, **6**, 605 (1923).
(3) H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955).

The conversion of diaryl thionocarbonates to the corresponding thiolcarbonates (the Schönberg rearrangement) has been shown by Tarbell and his collaborators[3,4] to proceed *via* a four-membered cyclic intermediate. These arrangements require temperatures in the range of 250–300°, while the rearrangement of allyl aryl thionocarbonates occur at room temperature.

The allylic shift associated with the rearrangement was demonstrated by both the infrared and n.m.r. spectra of the products. Compound I had a very weak band at 926 cm.$^{-1}$ and a medium band at 964 cm.$^{-1}$, corresponding to the —CH=CH— group.[5]

$$4\text{-ClC}_6\text{H}_4\text{OC(S)Cl} + \text{HOCH(CH}_3\text{)CH=CH}_2 \longrightarrow 4\text{-ClC}_6\text{H}_4\text{OC(O)SCH}_2\text{CH=CHCH}_3 \quad \text{(I)}$$

$$4\text{-ClC}_6\text{H}_4\text{OC(S)Cl} + \text{HOCH}_2\text{CH=CHCH}_3 \longrightarrow 4\text{-ClC}_6\text{H}_4\text{OC(O)SCH(CH}_3\text{)CH=CH}_2 \quad \text{(II)}$$

Compound II showed strong absorption at 923 cm.$^{-1}$ and had a moderately strong band at 985 cm.$^{-1}$, characteristic of the CH out-of-plane deformations of the vinyl group.[5] The other thiolcarbonates derived from 2-buten-1-ol and from allyl alcohol (Table III) had spectra similar to that of Compound II.

The nuclear magnetic resonance spectrum of compound I exhibited a doublet at 8.42 τ due to the methyl group, a doublet at 6.87 τ attributable to the methylene group, and a multiplet at 4.52 τ in agreement with the presence of two olefinic hydrogens. On the other hand, compound II exhibited a doublet at 8.57 τ, a multiplet centered at 5.92 τ due to a single hydrogen atom (the methine group), and a complicated signal extending from 4.14 τ to 4.77 τ, attributable to the three olefinic hydrogens of the vinyl group.

Additionally, it may be noted (Table III) that the refractive index n^{25}D, of I is greater than that of II by 0.00789. Examination of the refractive indices of a series of isomeric alkenes[6] indicates that the refractive indices of both *cis* and *trans* isomers of 2-alkenes are consistently higher than those of the isomeric 3-methyl-1-alkenes.

Both the infrared and n.m.r. spectra showed that all the 1-crotyl and 1-methylallyl esters in Table III were pure, containing no admixtures of the allylic isomer. The rearrangement is thus analogous to the conversion of allyl thiocyanates to isothiocyanates[7] which also involves an allylic shift.

A similar rearrangement has recently been reported[8] by Taguchi and Nakao, who indicate that S-methyl allylxanthate rearranges thermally to the corresponding dithiolcarbonate.

Although the esterification of ethanol, 2,2-dichloroethanol, and 2,2,2-trichloroethanol with 3,4-dichlorophenyl chlorothionoformate proceeded without rearrangement, the corresponding reaction with ethylenechlorohydrin yielded exclusively S-(2-chloroethyl) 3,4-dichlorophenyl thiolcarbonate (strong C=O absorption at 1727 cm.$^{-1}$). The product was characterized by hydrolysis to 3,4-dichlorophenol in quantitative yield. As in the case of the allyl derivatives, the intermediate thionocarbonate could not be isolated even under very mild reaction conditions.

Experimental[9]

Aryl Chlorothionoformates. 3,4-Dichlorophenyl Chlorothionoformate.—A solution of 3,4-dichlorophenol (40.7 g., 0.25 mole) in 1 *N* sodium hydroxide solution (250 ml., 0.25 mole) was added during 45 min. to a stirred solution of thiophosgene (28.7 g., 0.25 mole) in chloroform (200 ml.) at 25°. The mixture was stirred for 2 hr., and the layers were separated. The aqueous layer was extracted with chloroform (3 × 50 ml.) and the combined chloroform extracts were dried and evaporated. Distillation of the residue gave 3,4-dichlorophenyl chlorothionoformate, b.p. 98–100°/1.3 mm., yield 50.0 g. (83%). The distillate crystallized on standing, m.p. 58–60°.

The distillation residue was crystallized from dimethylformamide–methanol to give bis(3,4-dichlorophenyl) thionocarbonate, m.p. 137–138°, yield 3.2 g. (7.0%).

The new chlorothionoformates prepared by this method are described in Table I.

Diaryl Thionocarbonates. Bis(2,4,6-trichlorophenyl) Thionocarbonate.—Pyridine (15.6 g., 0.19 mole) was added dropwise to a solution of 2,4,6-trichlorophenol (30.9 g. 0.156 mole) and thiophosgene (8.9 g., 0.078 mole) in benzene (150 ml.). The mixture was refluxed for 20 min. and was then filtered hot. The benzene solution was washed with 10% sulfuric acid (4 × 100 ml.) and with water. The solution was dried and evaporated, and the residue was crystallized from dimethylformamide to give the product, m.p. 167–168°, yield 10.0 g. (29%).

4-*t*-Butylphenyl 3,4-Dichlorophenyl Thionocarbonate.—Pyridine (7.6 g., 0.99 mole) was added dropwise to a solution to 4-*t*-butylphenyl chlorothionoformate (10.0 g., 0.048 mole) and 3,4-dichlorophenol (7.8 g., 0.048 mole) at room temperature. The solution was refluxed for 30 min., and then cooled, washed with water, dried, and evaporated. The residue was crystallized from methanol to give the product, m.p. 89–91°, yield 11.4 g. (61%).

3,4-Dichlorophenyl 3-nitrophenyl thionocarbonate was similarly prepared from 3,4-dichlorophenol and 3-nitrophenyl chlorothionoformate.

Aryl Alkyl Thionocarbonates. 4-Chlorophenyl Ethyl Thionocarbonate.—4-Chlorophenyl chlorothionoformate (10.0 g., 0.048 mole) was refluxed in ethanol (50 ml.) for 1 hr. The solution was evaporated and the residue was fractionated, giving the product b.p. 88°/0.43 mm., yield 8.3 g. (79%).

4-Chlorophenyl *n*-Heptyl Thionocarbonate.—Pyridine (3.5 ml., 0.044 mole) was added dropwise to a mixture of 4-chlorophenyl chlorothionoformate (5.0 g., 0.024 mole) and *n*-heptyl alcohol (5.8 g., 0.05 mole) at 0°. After being al-

(4) D. H. Powers and D. S. Tarbell, *J. Am. Chem Soc.*, **70**, 70 (1956).

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(6) R. R. Dreisbach, "Physical Properties of Chemical Compounds (II)," American Chemical Society, Washington, D. C., 1959, p. 223 ff.

(7) P. A. S. Smith and D. W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

(8) T. Taguchi and M. Nakao, *Tetrahedron*, **18**, 245 (1962).

(9) All melting points are uncorrected. Microanalyses by Dr. C. Daesslé, Montreal, Quebec.

TABLE II

THIONOCARBONATES ROC(S)OR′

R	R′	Yield, %	B.p., °C./mm.	B.p., °C.	Formula	C Calcd.	C Found	H Calcd.	H Found	Cl Calcd.	Cl Found	S Calcd.	S Found
3,4-Dichlorophenyl	3,4-Dichlorophenyl	7[a]		137–138[h]	$C_{13}H_6Cl_4O_2S$	42.42	42.57	1.65	1.89	38.54	39.00	8.71	8.77
3,4-Dichlorophenyl	3-Nitrophenyl	8		147.5–148[i]	$C_{13}H_7Cl_2NO_4S$[l]	45.36	45.64	2.05	2.22	20.60	21.30	9.32	9.48
3,4-Dichlorophenyl	4-t-Butylpheny	61		89–91[j]	$C_{17}H_{16}Cl_2O_2S$	57.47	57.35	4.54	4.88	19.96	20.08	9.02	9.00
2-Chloro-4-nitrophenyl	2-Chloro-4-nitrophenyl	36[a]		177–178[j]	$C_{13}H_6Cl_2N_2O_5S$[m]	40.13	40.02	1.55	1.36	18.22	18.60	8.24	8.48
3-Chlorophenyl	3-Chlorophenyl	8[a]		106–108[j]	$C_{13}H_8Cl_2O_2S$	52.19	51.88	2.70	2.61	23.70	23.54	10.71	10.77
2,4,6-Trichlorophenyl	2,4,6-Trichlorophenyl	29		167–168[i]	$C_{13}H_4Cl_6O_2S$	35.73	35.83	0.92	1.24	48.64	48.34	7.34	7.28
3,4-Dichlorophenyl	Ethyl	35	105–106/0.25[b]		$C_9H_8Cl_2O_2S$	43.04	42.90	3.21	3.24	28.23	28.46	12.76	12.73
3,4-Dichlorophenyl	2,2-Dichloroethyl	80	125/0.1[c]		$C_9H_6Cl_4O_2S$	33.77	33.68	1.89	1.88	44.32	44.52	10.02	10.01
3,4-Dichlorophenyl	2,2,2-Trichloroethyl	57	134/0.17	57–58[j]	$C_9H_5Cl_5O_2S$	30.49	30.82	1.42	1.62	50.01	49.89	9.04	9.21
3-Chlorophenyl	2,2,2-Trichloroethyl	47		55–57[k]	$C_9H_6Cl_4O_2S$	33.77	33.55	1.88	1.79	44.32	44.12	10.01	10.31
4-Chlorophenyl	Ethyl	79	88/0.43[d]		$C_9H_9ClO_2S$	49.88	50.31	4.19	4.31	16.36	16.44	14.79	14.48
4-Chlorophenyl	*n*-Heptyl	73	160/0.2[e]		$C_{14}H_{19}ClO_2S$	58.62	58.91	6.67	6.82	12.36	12.82	11.17	11.22
4-Chlorophenyl	*n*-Decyl	62		45–47[j]	$C_{17}H_{25}ClO_2S$	62.08	61.82	7.66	7.46	10.78	10.78	9.74	10.00
4-Chlorophenyl	*n*-Tetradecyl	40		53–54.5[j]	$C_{21}H_{33}ClO_2S$	65.51	65.77	8.64	8.78	9.21	9.29	8.33	8.20
4-Chlorophenyl	*n*-Pentadecyl	42		56–57[j]	$C_{22}H_{35}ClO_2S$	66.22	66.28	8.84	8.34	8.88	8.87	8.04	7.89
4-Chlorophenyl	2,2,2-Trichloroethyl	30		72–73[j]	$C_9H_6Cl_4O_2S$	33.78	34.01	1.89	2.07	44.32	44.06	10.01	9.85
p-Tolyl	Ethyl	60	132–134/14[f]	40–42[k]	$C_{10}H_{12}O_2S$	61.19	61.05	6.16	6.11			16.33	16.34
p-Tolyl	6-(1-Hexenyl)	49	124/0.47[g]		$C_{14}H_{18}O_2S$	67.17	67.19	7.25	7.37			12.80	12.60
3-Nitrophenyl	2,2,2-Trichloroethyl	47		81–83[k]	$C_9H_6Cl_3NO_4S$[n]	32.69	32.68	1.82	1.73	32.17	32.38	9.69	9.84

[a] Isolated as by-product from the preparation of the corresponding chlorothionoformate. [b] $n^{25}D$ 1.56820, D^{20}_4 1.3650. [c] $n^{25}D$ 1.57640, D^{20}_4 1.4980. [d] $n^{25}D$ 1.55303, D^{20}_4 1.2675. [e] $n^{25}D$ 1.52600, D^{20}_4 1.1460. [f] $n^{25}D$ 1.53758, D^{20}_4 1.1070. [g] $n^{25}D$ 1.52903, D^{20}_4 1.0620. [h] Recrystallized from dimethylformamide–methanol. [i] Recrystallized from dimethylformamide–ethanol. [j] Recrystallized from methanol. [k] Recrystallized from petroleum ether. [l] Calcd.: N, 4.07. Found: N, 4.51. [m] Calcd.: N, 7.20. Found: N, 7.40. [n] Calcd. N, 4.23. Found: N, 4.30.

TABLE III

THIOLCARBONATES ROC(O)SR′

R	R′	Yield %	B.p., °C.	$n^{25}D$	D^{20}_4	Formula	C Calcd.	C Found	H Calcd.	H Found	Cl Calcd.	Cl Found	S Calcd.	S Found
3,4-Dichlorophenyl	2-Chloroethyl	35	135–136/0.2	1.56108	1.4360	$C_9H_7Cl_3O_2S$	37.85	37.61	2.47	2.48	37.24	37.48	11.25	11.55
3,4-Dichlorophenyl	Allyl	86	112–114/0.25	1.57130	1.3520	$C_{10}H_8Cl_2O_2S$	45.63	45.83	3.06	3.24	26.94	27.24	12.18	12.29
p-Tolyl	Allyl	78	118/1.95	1.54151	1.0953	$C_{11}H_{12}O_2S$	63.43	63.53	5.81	5.75			15.39	15.13
p-Tolyl	1-Methylallyl	39	107–108/0.7	1.53214	1.0972	$C_{12}H_{14}O_2S$	64.83	64.97	6.35	6.38			14.42	14.42
4-Chlorophenyl	Allyl	80	100–102/0.42	1.55686	1.2560	$C_{10}H_9ClO_2S$	52.51	52.50	3.97	3.80	15.50	15.70	14.02	14.22
4-Chlorophenyl	1-Methylallyl	72	118–119/0.75	1.54698	1.2120	$C_{11}H_{11}ClO_2S$	54.43	54.64	4.57	4.70	14.61	14.69	13.21	13.22
4-Chlorophenyl	1-Crotyl	73	110/0.2	1.55487	1.2034	$C_{11}H_{11}ClO_2S$	54.43	54.78	4.57	4.74	14.61	14.51	13.21	13.27
2-Chloro-4-nitrophenyl	1-Methylallyl	47	132–134/0.6	1.57026	1.3510	$C_{11}H_{10}ClNO_4S$[a]	45.92	45.58	3.50	3.42	12.32	12.61	11.15	11.09

[a] Calcd.: N, 4.87. Found: N, 4.67.

lowed to stand overnight at room temperature, the reaction mixture was extracted with ether (150 ml.). The ether solution was washed with 5% sodium hydroxide solution and with water, and then was dried and evaporated. The residue was fractionated, giving the product, b.p. 160°/0.2 mm., yield 5.1 g. (73%).

The aryl alkyl thionocarbonates described in Table II could be prepared by either of these procedures, except that when the alcohol was *n*-heptyl or higher, better results were obtained when the reaction was performed in the presence of pyridine.

Thiolcarbonates: S-Allyl *p*-Tolyl Thiolcarbonate.—A solution of *p*-tolyl chlorothionoformate (15.0 g., 0.081 mole) in allyl alcohol (15 g.) was refluxed for 2 hr. The solution was evaporated and the residue was fractionated, giving the product, b.p. 136–138°/10 mm., yield 13.2 g. (78%).

All of the thiolcarbonates listed in Table III could be prepared in this way.

S-(1-Methylallyl) *p*-Tolyl Thiolcarbonate.—*p*-Tolyl chlorothionoformate (12.1 g., 0.065 mole) was added to a solution of 2-buten-1-ol (14.0 g., 0.19 mole) in pyridine (20 ml.) at 10° over a period of 25 min. After being allowed to stand for 3 hr., the reaction mixture was diluted with ether (200 ml.). The ether solution was washed with 5% sodium hydroxide solution and with water, and was then evaporated at room temperature under reduced pressure to constant weight (5.65 g., yield 39%). A portion of the product was distilled (b.p. 107–108°/0.7 mm.) for analysis. Both the distilled and the undistilled fractions were analytically pure, and both had infrared spectra identical with that of the product prepared as described above.

S-(2-Chloroethyl) 3,4-dichlorophenyl thiolcarbonate was prepared by this procedure.

Hydrolysis of S-(2-Chloroethyl) 3,4-Dichlorophenyl Thiolcarbonate.—A suspension of the thiolcarbonate (14.25 g., 0.05 mole) in 1 *N* potassium hydroxide solution (150 ml.) was allowed to stand for 18 hr. The suspension was acidified and extracted with ether (3 × 100 ml.), and the ether extract was evaporated to dryness. Fractionation of the residue yielded 3,4-dichlorophenol, b.p. 98–100°/0.8 mm., yield 8.10 g. (99%). The product melted at 65–66° after recrystallization from petroleum ether (60–90°), and did not depress the melting point of a known sample.

Hydrolysis of S-(1-Methylallyl) 2-Chloro-4-nitrophenyl Thiolcarbonate.—A solution of the thiolcarbonate (0.485 g., 0.00169 mole) in 1 *N* aqueous potassium hydroxide (5.5 ml.) and methanol (15 ml.) was allowed to stand overnight. The solution was acidified and extracted with ether (3 × 50 ml.), and the ether extract was dried and evaporated. The residue was dried at 70°/20 mm., giving 2-chloro-4-nitrophenol, m.p. 107–109°, yield 0.259 g. (89%). There was no depression on admixture with a known sample.

The Nuclear Magnetic Resonance Spectra of Pentacyclic Triterpenes[1,2]

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The n.m.r. spectra of a series of pentacyclic triterpenoidal derivatives have been studied, and some correlations between structures and spectra have been made.

The present study of the n.m.r. spectra of pentacyclic triterpenes was initiated with the hope that the spectra obtained would help in the structural elucidation of new pentacyclic triterpenes, and perhaps assist in establishing the class to which a triterpene of unknown structure belongs.

The n.m.r. spectra of a series of pentacyclic triterpenes were studied using tetrachloroethylene as the solvent and chloroform (10%) as an internal standard. In order to have uniform and dependable results, the same amount of triterpene was almost always used (20 mg.), but in a few cases less than this quantity was employed because of a limited supply of the pure compound. The spectra were recorded at 40 megacycles/second with a Varian Associates High Resolution Nuclear Magnetic Resonance spectrometer equipped with a Varian Associates super-stabilizer. All absorptions were calibrated by the audiofrequency side band technique. *Values given for the chemical shifts are in parts per million, with tetramethylsilane taken as zero and chloroform as 7.25.*

In an effort to increase the solubility of the triterpenes and make the spectra more significant, most of the triterpenes were converted to their corresponding methyl ester acetate derivatives. Since the ursane, oleanane, and lupane series are the most widespread of the pentacyclic triterpenes found in nature, the majority of the triterpenes studied here belong to these three groups. A few triterpenes of unknown or of recently elucidated structure were included in the study. On p. 4513 are given the structures and conformations of α-amyrin (I and Ia), β-amyrin (II and IIa), and lupeol (III and IIIa), the simplest alcohols of the ursane, oleanane, and lupane series respectively.

Discussion

Some Characteristics of the N.m.r. Spectra of Pentacyclic Triterpenes.—Many distinct absorptions can be found in the spectra of pentacyclic triterpenes. Methyl esters and acetoxyl groups give sharp absorptions.[5] Angular methyl groups also give well defined absorptions. However, since pentacyclic triterpenes contain a number of

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