CLEAVAGE OF SUBSTITUTED DISPIRO[BIS(3'-AMINOINDENE)-1',4;1',5-(1,3-DITHIOLANES)] BY MEANS OF TRANSITION METAL SALTS*

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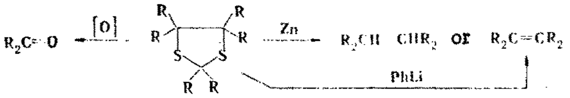
Dispiro[bis(3-aminoindene)-1',4;1',5-(1,3-dithiolanes)] react readily with Cu^+, Ag^+, Hg^+, and Hg^{2+} salts to give the corresponding bis(1-imino-3-indenyls) and methanedithiol derivatives. Bis(1-oxo-3-indenyls) are formed when the reaction is carried out in the presence of water. The reactivities of the 1,3-dithiolanes were examined with allowance for electronic and steric factors, and the reactivities of the metal cations were examined from the point of view of Pearson's theory. Methods for the alternative synthesis of the compounds obtained were found, and their IR and PMR spectra are discussed.

The available methods for cleavage of 1,3-dithiolanes in order to prove their structures or to solve problems of fine organic synthesis are diverse [2-6]. The reductive desulfuration of these compounds is realized by means of zinc in hydrochloric and acetic acids or by means of Raney nickel [4]. 1,3-Dithiolanes are unstable with respect to the action of sodium dichromate in acetic acid [3] or to the action of phenyllithium [5, 6]. The compounds formed as a result of these reactions are presented in the following scheme:



No data on the cleavage of 1,3-dithiolanes under the influence of transition metal salts are available. Our attempt to cleave 4,4,5,5-tetraphenyl-1,3-dithiolane by means of Ag^+ and Hg^+ ions was unsuccessful. It is known only that aldehydes are formed in the reaction of dialkylmercaptals with mercuric chloride in aqueous media [7].

Our recently obtained [8] dispiro[bis(3'-aminoindene)-1',4;1',5-(1,3-dithiolanes)] (I), which contain a reactive aminoindene grouping of atoms, form difficult-to-separate mixtures of compounds in the case of reaction with the usual desulfuration agents [2-6]. However, in contrast to the previously known 1,3-dithiolanes [2-6], spiroindene-substituted dithiolanes I react readily with CuCl, $AgNO_3$, $Hg(NO_3)_2$, and $HgCl_2$ in dimethylformamide (DMF) at 20 deg C; the products are slightly soluble methanedithiol salts of the II type (see the experimental section) and deeply colored solutions of the hypothetical 3,3'-diindenyl-1,1'-diimmonium salts (III). The corresponding crystalline bases – bis(1-arylimino-2-phenyl-3-indenyls) (IV) – were obtained from solutions of N- and 2-diaryl-substituted salts IIIb-d, which are most stable with respect to hydrolysis (see [9]). In the presence of water, salts IIIa,e-i, which have substitution of a different character at the nitrogen and C_2 salts, are hydrolyzed rapidly to give bis[1-dioxo-2-aryl(alkyl)-3-indenyls] (V). The latter were also isolated in the hydrolysis of bases IV with mineral acids.

The structural analogs of I – dispiro[(3'-piperidino-2'-phenylindene)-1',4-(1,3-dithiolane)-1",5-(3"-oxo-2"-phenylindane)] (VI) and dispiro[bis(3'-oxo-2'-phenylindane)-1',4;1',5-(1,3-dithiolane)] (VII) [8] – are also capable of cleavage under the influence of silver or mercury salts. However, their reactivities in this type of transformation are considerably lower and can be represented by the series VII ≪ VI ≪ I (see the experimental section). The increased reactivities of dithiolanes I are evidently due to the presence in the mole-

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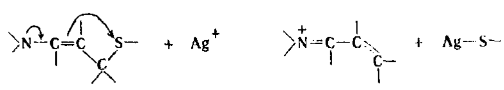
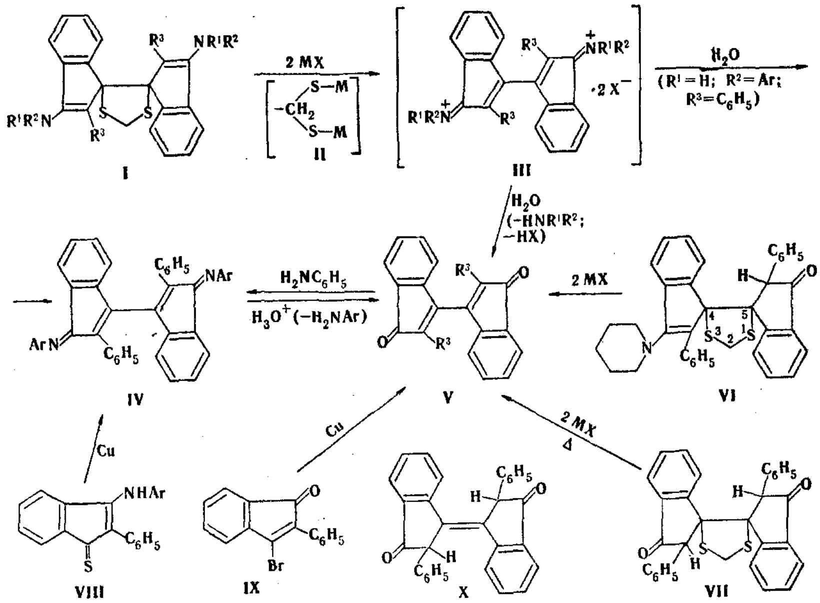
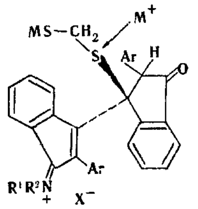
cules of these compounds of an amino allyl sulfide grouping of atoms, which leads to increased nucleophilicity of the sulfur atoms and to stabilization of the intermediately formed carbonium ion:



In addition, there are differences in the steric shielding of the sulfur atoms in I and VII (2-phenylindene and 2-phenylindane fragments, respectively), and this also may affect the rate of the reaction under discussion. With respect to its reactivity, VI occupies an intermediate position between dithiolanes I and VII. The presence of one amino allyl sulfide grouping facilitates electrophilic attack on the S-3 atom of the dithiolane ring. In the transition state the S-1 atom turns out to be under similar conditions from the point of view of the electronic factors as the sulfur atoms of dithiolane VII but in a more favorable (for attack by the M^+ ion) orientation from the point of view of the steric factor (disappearance of one spiro atom):



$MX = CuCl$; $AgNO_3$; $HgNO_3$; $Hg(NO_3)_2$; $HgCl_2$; I, III **a** $R^1, R^2 = H, R^3 = C_6H_5$; **b** $R^1 = H, R^2, R^3 = C_6H_5$; **c** $R^1 = H, R^2 = 4\text{-}ClC_6H_4, R^3 = C_6H_5$; **d** $R^1 = H, R^2 = 4\text{-}CH_3OC_6H_4, R^3 = C_6H_5$; **e** $R^1 = H, R^2 = C_6H_5, R^3 = C_2H_5$; **f** $R^1, R^2 = -(CH_2)_5, R^3 = 4\text{-}CH_3OC_6H_4$; **g** $R^1, R^2 = -(CH_2)_5, R^3 = C_6H_5$; **h** $R^1, R^2 = -(CH_2)_5, R^3 = 1\text{-}C_{10}H_7$; **i** $R^1, R^2 = -(CH_2)_2O(CH_2)_2, R^3 = C_6H_5$; IV, VIII **a** $Ar = C_6H_5$; **b** $Ar = 4\text{-}ClC_6H_4$; **c** $Ar = 4\text{-}CH_3OC_6H_4$; V **a** $R^3 = C_2H_5$; **b** $R^3 = C_6H_5$; **c** $R^3 = 4\text{-}CH_3OC_6H_4$; **d** $R^3 = 1\text{-}C_{10}H_7$



Of the investigated metal cations, only Cu^+, Ag^+, Hg^+, and Hg^{2+} undergo reaction with 1,3-dithiolanes I. The Fe^{3+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} salts do not react with dithiolanes I.* These data are satisfactorily interpreted by means of Pearson's theory of hard and soft acids and bases [10]. Since the first step in the cleavage is electrophilic attack by the metal cation on a "soft" base – the sulfur atom [11] of the dithiolane ring – only cations in the "soft" acid category undergo reaction.

A peculiarity of dithiolanes I, VI, and VII as compared with dithiolanes described in the literature is the presence of an activated hydrogen atom in the α position of the substituent attached to the heteroring (for VI and VII) or an enamine grouping (for I and VI). This ensures stabilization of the intermediately formed cation by ejection of a proton or the formation of an immonium fragment. 1,3-Dithiolanes (such as the above-mentioned 4,4,5,5-tetraphenyl-1,3-dithiolane), in the molecules of which stabilization of the carbonium ion cannot be realized, are not capable of cleavage by transition metal salts.

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*Other salts were not used in the given reaction.

The structure of IV was confirmed by their IR spectra ($\nu_{C=N}$ 1640 cm^{-1}) and also by chemical means. Bis(1-phenylimino-2-phenyl-3-indenyl) IVa is formed in high yield when Vb is refluxed in aniline in the presence of catalytic amounts of p-toluenesulfonic acid. 3-Arylamino-2-phenylindene-1-thiones VIII form the corresponding diindenyls IV in 80-90% yields when they react with copper in refluxing DMF. A similar transformation has been described for 4-thioacridone [12].

A triplet for protons of a CH_3 group (1.07 ppm) and a quartet for protons of a methylene group (2.27 ppm, $^3J_{CH_2CH_3}$ = 7 Hz) are observed in the PMR spectrum of bis(1-oxo-2-ethyl-3-indenyl) Va; a multiplet at 6.65-7.58 ppm is observed for the protons of the aromatic rings. Only signals of aromatic protons at 6.42-7.72 ppm are observed in the PMR spectrum of Vb. Thus the X structure previously proposed [13] for diketone Vb is repudiated on the basis of the PMR spectra.

Bis(1-oxo-2-phenyl-3-indenyl) (Vb) has been described in the literature [14]. It has been shown that it is formed in low yields from 2,2-bis(phenylethynyl)tolan and in the reaction of 3-bromo-2-phenylindenone with copper. The compound obtained in [14] has similar absorption in its IR spectrum ($\nu_{C=O}$) but has a different melting point than Vb (see Table 1). We have shown that Vb is formed in low yield (~5%) in the reaction of 3-bromo-2-phenylindenone IX with copper in refluxing DMF. It was characterized by means of thin-layer chromatography (TLC) with the use of various eluents and adsorbents. It cannot be isolated in the pure state by the method in [14]. Thus the depressed melting point of Vb presented in [4] is evidently due to the insufficient purity of the isolated compound.

EXPERIMENTAL*

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of 10% solutions of the compounds in CCl_4 were recorded with a Tesla BS 487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

1,3-Dithiolanes I were obtained by the method in [8]. Of these, dispiro{bis[1'-(4-chlorophenyl)amino-2'-phenylindene]-1',4;1',5-(1,3-dithiolane)} (Ic) [82%, mp 194-200 deg C (dec.)] was characterized for the first time. Found: Cl 10.0; N 3.8; S 9.1%. $C_{43}H_{30}Cl_2N_2S_2$. Calculated: Cl 10.0; N 4.0; S 9.0%. Also characterized for the first time was dispiro{bis[1'-(4-methoxyphenyl)-2'-phenylindene]-1',4;1',5-(1,3-dithiolane)} (Id) [78%, mp 145-151 deg C (dec.)]. Found: C 77.0; H 5.2; N 4.0; S 8.9%. $C_{45}H_{36}N_2O_2S_2$. Calculated: C 77.1; H 5.2; N 4.0; S 9.1%).

Bis(1-arylimino-2-aryl-3-indenyls) (IV). A) A solution of 0.5 g of silver nitrate in 5 ml of DMF was added to a solution of 0.5 g of dithiolane Ib-d in 10 ml of dry DMF, and the mixture was stirred for 5 min. The precipitated orange (light-yellow in the case of $HgCl_2$) II (0.6 g) was removed by filtration. Compounds II are insoluble in water and ordinary organic solvents, and they therefore could not be prepared in the analytically pure state. They were slowly decomposed by refluxing concentrated hydrochloric acid to give the chloride of the corresponding metal and a readily volatile substance with an unpleasant odor. The silver derivatives darkened rapidly on storage. IR spectra: 2885-2970 (w), ν_{CH_2}; 1390, δCH_2; 700-840 (w), ν_{C-S}, δ_{CH_2}; other bands were not present in the 500-3400 cm^{-1} region. The mother liquor after separation of dithiolate II was poured into 50 ml of water, and the precipitated IV was removed rapidly by filtration (see Table 1 for the yields). The products were recrystallized from hexane–benzene (3:1).

B) A mixture of 0.15 g of Vb, 10 ml of aniline, and 0.01 g of p-toluenesulfonic acid was refluxed for 10 h, after which it was cooled and treated with 10 ml of methanol, and 0.18 g (88%) of diindenyl IVa was removed by filtration.

C) A mixture of 1.2 g of amino thione VIII, 1.5 g of activated copper powder [15], and 15 ml of dry DMF was refluxed for 1 h in an inert atmosphere, another 1.5 g of copper powder was added, and the mixture was refluxed for another hour. It was then cooled and filtered, and the mother liquor was treated with 100 ml of water. The mixture was filtered to give 0.95 g (89%) of diindenyl IVa, 0.77 g (71%) of diindenyl IVb, and 0.98 g (90%) of diindenyl IVc.

Bis(1-oxo-2-aryl-3-indenyls) (V). A) A mixture of 0.5 g of dithiolane I, 20 ml of methanol, and 2 ml of a saturated aqueous solution of $AgNO_3$ was stirred at 20 deg C for 1 min, and the resulting precipitate was removed rapidly by filtration. The corresponding diketone V crystallized slowly from the mother liquor (see Table 1 for the yields). The diketones were recrystallized from benzene–methanol (1:3). Diketone Va was

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*Silver nitrate was used in the cleavage methods presented. Solutions of CuCl, $HgNO_3$, $Hg(NO_3)_2$, and $HgCl_2$ can be used in place of it. The yields of products remain virtually unchanged.

TABLE 1. Properties of the Synthesized Bisindenyls IV and V

Compound	R^3	mp, deg C	Found, %			Empirical formula	Calc., %			Yield by method A
			C	H	N		C	H	N	
IVa	C_6H_5	300—302	89,7	5,0	4,7	$C_{42}H_{28}N_2$	90,0	5,0	5,0	93
IVb	C_6H_5	240—242	Cl 11,5	—	4,5	$C_{42}H_{26}Cl_2N_2$	Cl 11,3	—	4,5	92
IVc	C_6H_5	214—217	85,1	5,3	4,4	$C_{44}H_{32}N_2O_2$	85,3	5,2	4,5	95
Va	C_2H_5	198—202	84,1	5,7	—	$C_{22}H_{18}O_2$	84,1	5,7	—	60
Vb	C_6H_5[a]	237—238[b]	87,7	4,4	—	$C_{30}H_{18}O_2$	87,8	4,4	—	99
Vc	4-$CH_3OC_6H_4$	219—220	81,7	4,9	—	$C_{32}H_{22}O_4$	81,7	4,7	—	92
Vd	1-$C_{10}H_7$[c]	229—231	89,3	4,4	—	$C_{38}H_{22}O_2$	89,4	4,3	—	90

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a) The bis(2,4-dinitrophenylhydrazone), with mp 350–352 deg C, was obtained in 97% yield for Vb by the method in [16]. Found: C 65.5; H 3.4; N 14.6%. $C_{42}H_{26}N_8O_8$. Calculated: C 65.5; H 3.4; N 14.6%. b) This compound had mp 215–230 deg C (dec.) [14]. c) A crystal solvate with the composition $3C_{38}H_{22}O_2 \cdot 2CHCl_3$ was obtained by crystallization from chloroform. Found: C 78.7; H 3.9; Cl 12.4%. Calculated: C 78.3; H 3.9; Cl 12.4%.

obtained as a light-yellow crystalline substance, and diketones Vb-d were obtained as bright-red crystals that were readily soluble in benzene and chloroform, only slightly soluble in alcohol, and insoluble in water. IR spectrum: 1705 (C=O); 1590 and 1490 cm^{-1} (C=C).

B) A mixture of 0.5 g of diindenyl IV, 10 ml of methanol, and 1 ml of concentrated HCl was refluxed for 30 min, after which 5 ml of water was added, and the mixture was cooled. The crystalline precipitate of the corresponding ketone was then removed by filtration. The yields were quantitative.

C) A mixture of 0.1 g of dithiolane VI, 20 ml of methanol–dioxane (1 : 1), and 0.2 g of silver nitrate was refluxed for 30 min (or stirred at 20 deg C for 1 day), after which it was filtered, and 10 ml of water was added to the filtrate. The resulting red crystals of diketone Vb were removed by filtration. The yield was 30%. A slight amount of starting dithiolane was present in the reaction product (according to TLC) when the reaction was carried out at 20 deg C.

D) A mixture of 0.5 g of dithiolane VII, 0.5 g of crystalline silver nitrate, and 15 ml of butyl alcohol was refluxed for 36 h, and the resulting black precipitate was removed by filtration. Methanol (20 ml) was added to the mother liquor, and the next day 0.35 g of red crystals of a mixture of starting dithiolane VII and bisindenyl V was removed by filtration. The mixture was dissolved in chloroform and chromatographed with a column filled with activity II Al_2O_3. The substance in the first layer (red) from the bottom was eluted, and the solvent was removed from the eluate by evaporation to give 0.11 g (26%) of diketone Vb.

E) A 1-g sample of 3-bromo-2-phenylindenone IX was refluxed in DMF with activated copper powder, and the mixture was treated as in [14]. Diketone Vb was detected in the reaction products by TLC.

LITERATURE CITED

1. L. V. Timokhina, Ya. S. Tsetlin, E. O. Tsetlina, V. A. Usov, and M. G. Voronkov, Zh. Org. Khim., 15, 82 (1979).
2. E. Bergmann, M. Magat, and D. Wagenberg, Ber., 63, 2576 (1930).
3. A. Schonberg, B. Konig, and E. Singer, Ber., 100, 767 (1967).
4. A. Schonberg and S. Nickel, Ber., 64, 2323 (1931).
5. A. Schonberg, M. Elkaschef, M. Nosseir, and M. Sidky, J. Amer. Chem. Soc., 80, 6312 (1958).
6. F. Sondheimer and S. Wolfe, Can. J. Chem., 37, 1870 (1959).
7. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 3, Wiley.
8. N. A. Korchevin, V. A. Usov, E. O. Tsetlina, V. A. Pestunovich, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 1, 36 (1978).
9. Ya. F. Freimanis, The Chemistry of Enamino Ketones, Enamino Imines, and Enamino Thiones [in Russian], Zinatne, Riga (1974), p. 224.
10. Tse-Lok Ho, Chem. Rev., 75, 1 (1975).
11. J. F. W. McOmie, (editor), Protective Groups in Organic Chemistry [Russian translation], Mir, Moscow (1976), p. 248.

12. K. Lehmstedt and H. Haudertmark, Ber., 63, 1229 (1930).
13. N. A. Korchevin, V. A. Usov, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 5, 713 (1974).
14. B. J. Whitlock and H. W. Whitlock, J. Org. Chem., 37, 3559 (1972).
15. C. A. Buehler and D. E. Pearson, Survey of Organic Syntheses, Wiley, New York (1970).
16. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 1, Wiley.

REACTION OF AZIRIDINES WITH ACETYLENIC γ-HYDROXY ALDEHYDES

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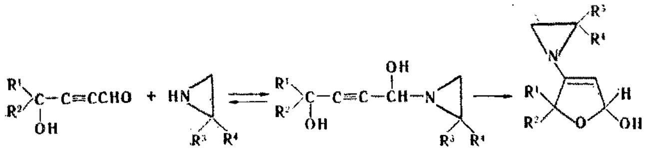
The corresponding acetylenic aziridino hydroxy carbinols were obtained by the reaction of aziridine, 2,2-dimethylaziridine, and methyl aziridine-2-carboxylate with 4-hydroxy-4-methylpent-2-yn-1-al and 3-(1-hydroxycyclohexyl)prop-2-yn-1-al. It is shown that the latter at room temperature undergo isomerization with time to 2-hydroxy-4-aziridino-5,5-dialkyldihydrofurans. The isomerization of acetylenic aziridinocarbinols, which includes an intermediate step involving retrodecomposition of the aziridino(hydroxy)carbinols to the starting aldehydes and aziridines, was investigated by dynamic NMR spectroscopy.

We have previously shown [1] that the reaction of 1-H-aziridines with propargyl and phenylpropargyl aldehydes gives acetylenic α-aziridinocarbinols, which are isomerized to β-aziridinoacroleins at room temperature. The mechanism of the isomerization, which includes an intermediate step involving the retrodecomposition of the acetylenic aziridinocarbinols to the starting aldehydes and aziridines with subsequent formation of β-aziridinoacroleins, was established.

To confirm the general character of the reactivities of 1-H-aziridines with α-acetylenic aldehydes and to ascertain the limits of the applicability of this reaction in the synthesis of acetylenic α-aziridinocarbinols and β-aziridinoacroleins we investigated the reaction of aziridines with acetylenic γ-hydroxy aldehydes. It is known [2] that 2-methoxy-4-dialkylaminodihydrofurans are formed in the reaction of secondary amines with acetylenic γ-hydroxy aldehydes in anhydrous methanol. However, the reaction is accompanied by resinification when it is carried out in absolute benzene or ether.

As a result of the study it was shown that the reaction of aziridine (IIIa), and 2,2-dimethyl- (IIIb) and 2-carbomethoxyaziridine (IIIc) with acetylenic γ-hydroxy aldehydes (I, II) in absolute ether at −30 deg C gives acetylenic aziridino(hydroxy)carbinols IVa–c and Va–c. The latter are colorless crystalline compounds, the physicochemical characteristics of which are presented in Table 1.


I, II III a–c IV–V a–c VI–VII a–c

I, IV, VI $R^1=R^2=CH_3$; II, V, VII $R^1-R^2=-(CH_2)_5-$; III–VII a $R^3=R^4=H$; b $R^3=R^4=CH_3$;
c $R^3=H$, $R^4=COOCH_3$

The IR spectra of acetylenic aziridino(hydroxy)carbinols IVa–c and Va–c are characterized by absorption bands of the stretching vibrations of a hydroxy group at 3300–3400 cm^{-1}, absorption maxima of a triple bond at 2240–2260 cm^{-1}, and C–H stretching vibrations of the aziridine ring at 3070–3080 cm^{-1}. No bands are present in the region characteristic for the absorption of conjugated C=O and C=C bonds.

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