[CONTRIBUTION FROM THE SAMUEL C. HOOKER LABORATORY OF THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Organic Sulfur Compounds. VIII.[1] Introduction of Oxygen in the Raney Nickel Desulfurization of Hemithioketals (1,3-Oxathiolanes)[2]

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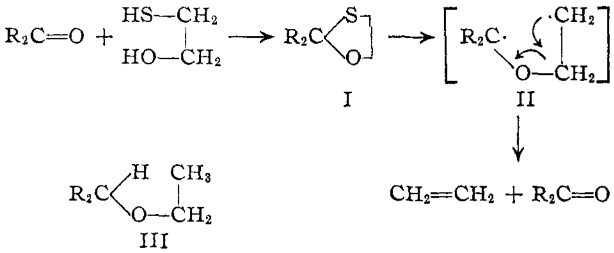
As demonstrated by several examples, the desulfurization of β-mercaptoethanols with Raney nickel in acetone solution proceeds as shown in reaction A, the main product being the alcohol. Desulfurization of the corresponding hemithioketals (1,3-oxathiolanes) under the same conditions involves introduction of oxygen from an outside source according to the reaction B. The use of optically active compounds demonstrated complete retention of configuration of the starred carbon atom.

The initial observation[3] that hemithioketals (I), readily obtainable[4] by the condensation of ketones with β-mercaptoethanol, upon desulfurization with Raney nickel regenerate the ketone rather than yield the expected ethyl ether (III) was explained[3] by assuming the decomposition of an intermediate 1,4-diradical II, the other product presumably being ethylene.

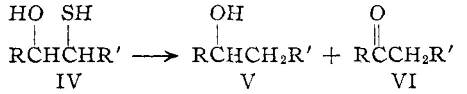


This reaction is of some preparative significance since it permits the use of a protective grouping for ketones which can be removed subsequently under neutral conditions and it has been employed for such purposes in the steroid series.[5] It was felt that a more detailed study of the mechanism of this reaction might shed some light on the general Raney nickel desulfurization process and it was essential, therefore, to isolate the other fragment (ethylene?) produced in the reduction of hemithioketals (I). In order to simplify the isolation problem, a series of substituted β-mercaptoethanols had been synthesized[1] and converted to hemithioketals which were employed as substrates for the desulfurization studies to be reported in this paper. Concurrently, there also has been investigated the course of the desulfurization of β-mercaptoethanols and these results will be considered first.

Desulfurization of β-Mercaptoethanols

It was anticipated that desulfurization of β-mercaptoethanols with Raney nickel catalyst[6] would proceed by reductive removal of the sulfur and formation of the corresponding alcohol. Experimentally it was shown that in acetone or ethyl methyl ketone solution, the alcohol was the major product, but that it was always accompanied by appreciable amounts of the corresponding ketone. In other solvents such as ethanol or benzene, the primary reaction products underwent further reduction or oxidation which had to be taken into account in the interpretation of the experimental results.

When 1,1-diphenyl-3-mercaptopropan-2-ol (IV)[1] was heated for 24 hours in refluxing ethyl methyl ketone solution with fresh Raney nickel catalyst, conditions which were required for the important desulfurization of the corresponding hemithioketal (XXIII) (*vide infra*), 55% of 1,1-diphenylpropan-2-ol (V) and 24% of 1,1-diphenylacetone (VI) were isolated. Similar treatment of the alcohol V led to quantitative recovery while the ketone VI was practically unchanged, less than 7% of the alcohol V being formed from it under those conditions. It follows, therefore, that the two desulfurization products are most likely not formed to any significant extent from each other by either reduction or oxidation.



$$\underset{\text{IV}}{\overset{\text{HO SH}}{\text{RCHCHR}'}} \longrightarrow \underset{\text{V}}{\overset{\text{OH}}{\text{RCHCH}_2\text{R}'}} + \underset{\text{VI}}{\overset{\text{O}}{\overset{\|}{\text{RCCH}_2\text{R}'}}} \quad \text{(A)}$$

$$R = (C_6H_5)_2CH\text{–},\ R' = H$$

Similar results were encountered with 2β-mercaptocholestan-3β-ol (VII),[1,7] which yielded a mixture of cholestan-3β-ol (VIII) and cholestan-3-one (IX) when refluxed in acetone solution with Raney nickel; control experiments with the two products VIII and IX demonstrated their stability under such conditions. Of considerable interest is the observation that when the desulfurization of 2β-mercaptocholestan-3β-ol (VII) was carried out in benzene solution in the rigorous absence of ethanol,[8] only cholestan-3-one (IX) was isolated. That this was probably due to oxidation of initially formed cholestan-3β-ol (VIII) was shown by the isolation of over 80% of cholestan-3-one (IX) when cholestan-3β-ol (VIII) was refluxed in benzene solution with ten times its weight of Raney nickel catalyst. Oxidation of saturated[9] and allylic[10] alcohols

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[1] Paper VII, C. Djerassi, M. Gorman, F. X. Markley and E. B. Oldenburg, THIS JOURNAL, **77**, 568 (1955).

[2] This work was carried out under contract No. DA-20-018-ORD-13474 with the Office of Ordnance Research, U. S. Army.

[3] J. Romo, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 4961 (1951).

[4] C. Djerassi and M. Gorman, *ibid.*, **75**, 3704 (1953).

[5] *Cf.* C. Djerassi, F. Batres, J. Romo and G. Rosenkranz, *ibid.*, **74**, 3634 (1952).

[6] W-2 Raney Nickel catalyst, prepared according to R. Mozingo (*Org. Synth.*, **21**, 15 (1941)), was employed in all of these studies. The age of each catalyst batch is given in the experimental section.

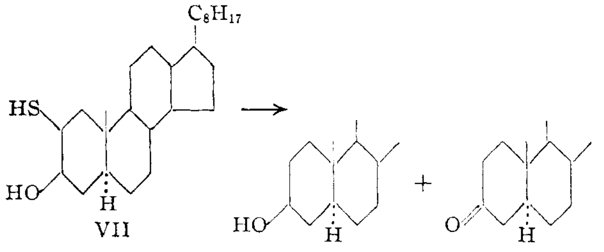
[7] The earlier assignment of configuration (footnote 9 in reference 1) was confirmed by the desulfurization of its diacetate to cholestan-3β-ol acetate.

[8] The removal of ethanol is indispensable. Thus, cholestan-3-one is reduced completely when refluxed with Raney nickel in ethanol solution and even small amounts of ethanol present in the benzene will prevent the oxidation (see Experimental for desulfurization of IV under such conditions).

[9] E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948); *cf.* M. R. Ehrenstein, A. R. Johnson, P. C. Olmsted, V. I. Vivian and M. A. Wagner, *ibid.*, **15**, 264 (1950).

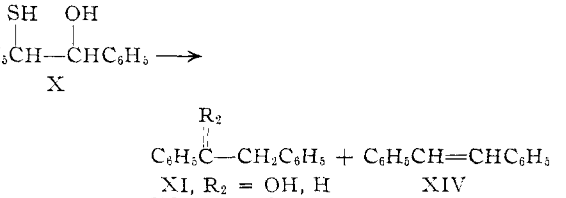
[10] J. Romo, *Bol. inst. quim. Mexico*, **4**, 91 (1952).

with Raney nickel in the presence of such hydrogen acceptors as cyclohexanone[9] and acetone[10] is known, but it was quite unexpected to observe such smooth oxidation of a saturated alcohol (VIII) in benzene solution under conditions where the presumably much better hydrogen acceptor acetone led to total recovery of the starting material. A more detailed study of the scope and mechanism of this oxidation appears warranted.



VII VIII IX

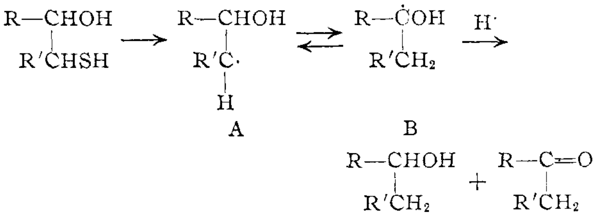
The course of the desulfurization of 1,2-diphenyl-2-mercaptoethanol (X)[1] proved to be somewhat more complex. Under standard conditions in acetone solution, 1,2-diphenylethanol (XI), desoxybenzoin (XII) and 1,2-diphenylethane (XIII) were isolated, while older Raney nickel samples (in benzene solution) or a reduced reaction time yielded some stilbene (XIV) together with the first two substances. The formation of some of these products is due to benzyl activation and some of the interconversions possible under these conditions are exemplified by the following control experiments. Stilbene (XIV) was reduced by fresh Raney nickel in acetone solution to 1,2-diphenylethane (XIII) and the latter, together with desoxybenzoin (XII), was formed when 1,2-diphenylethanol (XI) was refluxed in acetone solution with Raney nickel. Hydrogenolysis of benzyl alcohols has been observed previously[11] and when acetone was substituted by ethanol,[11] 1,2-diphenylethane (XIII) was formed exclusively from 1,2-diphenylethanol (XI). Allylic alcohols are known to be oxidized[10] by Raney nickel in acetone solution and the same behavior is to be expected from benzyl alcohols, as indeed proved to be the case with 1,2-diphenylethanol (XI).



$$\underset{\text{X}}{C_6H_5\overset{\overset{SH}{|}}{C}H-\overset{\overset{OH}{|}}{C}HC_6H_5} \longrightarrow C_6H_5\overset{\overset{R_2}{\|}}{C}-CH_2C_6H_5 + \underset{\text{XIV}}{C_6H_5CH{=}CHC_6H_5}$$

XI, R_2 = OH, H
XII, R_2 = O
XIII, R_2 = H_2

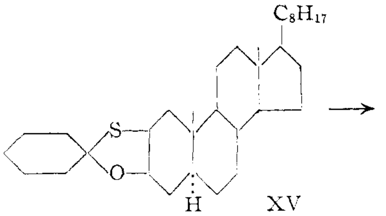
In summary, the "normal" course of the Raney nickel desulfurization of β-mercaptoethanols involves the formation of the corresponding alcohol accompanied by some ketone, both products presumably being formed by independent paths, unless extraneous factors (*e.g.*, benzyl activation) enter into the reaction. Accepting a free radical mechanism[12] for this process, the formation of both products could be rationalized by assuming a 1,2-shift of the intermediate free radical. Whether the alcohol is generated from A and/or B probably could be clarified by studying the desulfurization of an optically active β-mercaptoethanol.



$$\underset{R'CHSH}{\overset{R-CHOH}{|}} \longrightarrow \underset{\text{A}}{\underset{H}{\overset{R-CHOH}{R'\dot{C}}}} \rightleftarrows \underset{\text{B}}{\overset{R-\dot{C}OH}{R'CH_2}} \xrightarrow{H\cdot} \overset{R-CHOH}{R'CH_2} + \overset{R-C{=}O}{R'CH_2}$$

Desulfurization of Hemithioketals

The availability[1] of substituted mercaptoethanols and hence also of hemithioketals permitted the identification of all of the major products formed in the desulfurization of such substances. The first case investigated was the hemithioketal XV, formed from cyclohexanone and 2β-mercaptocholestan-3β-ol (VII), the expected products being cyclohexanone and Δ^2-cholestene (or cholestane formed by further reduction) if the plausible mechanism outlined in the introduction of this paper indeed obtains. Desulfurization in the standard manner (refluxing with ten times the weight of Raney nickel in acetone solution for 5 hours) yielded *ca.* 64% of cyclohexanone, 21% of cholestan-3-one (IX) and 60% of cholestan-3β-ol (VIII); no oxygen-free steroid was encountered in the chromatographic separation. *It is clear, therefore, that oxygen must have been introduced from an outside source during the reductive desulfurization process.*



XV

64%
+ VIII (60%)
+ IX (21%)

In order to show that this was not an exception but a general phenomenon, several other substituted hemithioketals were examined under the same conditions. Desulfurization of 2,3-diphenyl-1-oxa-4-thiaspiro[4,5]decane (XVI)[1] followed by steam distillation furnished 70% of cyclohexanone, while chromatography of the non-volatile portion yielded 42% of 1,2-diphenylethanol (XI), 11% of desoxybenzoin (XII) and 7% of stilbene (XIV). It should be noted that qualitatively, this mixture is quite similar to that encountered in the desulfurization of 1,2-diphenyl-2-mercaptoethanol (X). Desulfurization of spiro-(4-phenyl-1,3-oxathiolane-2,-3'-cholestane) (XVII)[1] was complete in 45 minutes, presumably due to benzyl activation, and led to 43% of β-phenethyl alcohol (XVIII) and 56% of cholestan-3-one (IX); the presence of phenylacetaldehyde (XIX) was indicated by infrared examination.

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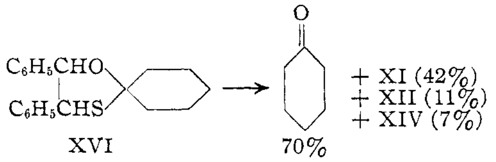
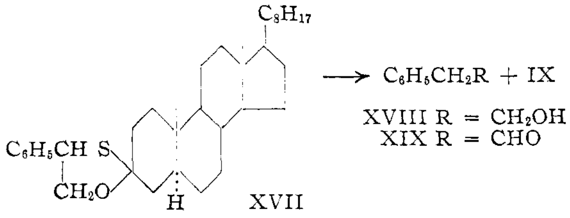
[11] W. A. Bonner, J. A. Zderic and G. A. Casaletto, THIS JOURNAL, **74**, 5086 (1952).

[12] Evidence for a free radical mechanism in the Raney nickel desulfurization of sulfides has been presented *inter alia* by W. A. Bonner (*ibid.*, **74**, 1034 (1952)), and by H. Hauptmann, B. Wladislaw, L. L. Nazario and W. F. Walter (*Ann.*, **576**, 45 (1952)).

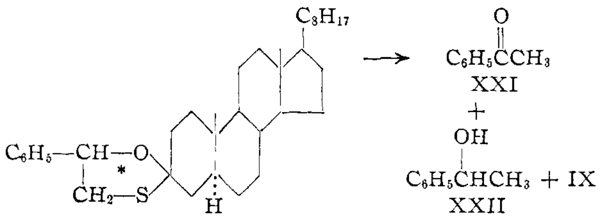


XVI



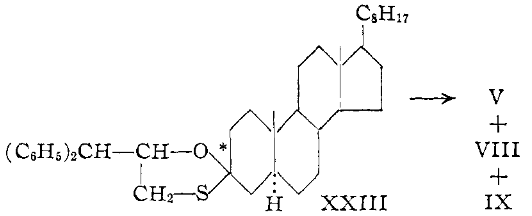
XVII

A particularly interesting case is spiro-(5-phenyl-1,3-oxathiolane-2,3′-cholestane) (XX),[1] formed from cholestan-3-one (IX) and 1-phenyl-2-mercaptoethanol. Since the optically inactive mercaptoethanol in this instance possesses an asymmetric carbon atom, four diastereoisomeric hemithioketals are possible and one of them was obtained[1] in a pure form. The anticipated products, cholestan-3-one (IX), acetophenone (XXI) and phenylmethylcarbinol (XXII) were indeed isolated, the latter compound *via* its 3,5-dinitrobenzoate ester. If the starred bond in XX is not affected in the desulfurization, the resulting alcohol XXII should be optically active. Unfortunately, the results proved to be quite erratic, the specific rotation of the dinitrobenzoate[13] of XXII ranging from +7 to 0° in various runs. Since this inconclusive result was probably due to racemization of the labile benzyl alcohol type, an example was selected where such activation (by an adjacent aromatic ring) was not possible and which would give an unambiguous answer to this important question.



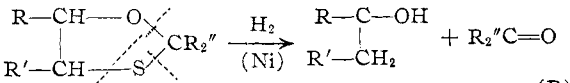
XX

The substituted mercaptoethanol selected was 1,1-diphenyl-3-mercaptopropan-2-ol (IV), since the expected desulfurization products V and VI are solids. Condensation of this mercaptoethanol with cholestan-3-one (IX) can give rise theoretically to four possible diastereoisomeric forms of the hemithioketal XXIII and three of them were isolated in a pure state. Consequently, two of these must be derived from enantiomeric 1,1-diphenyl-3-mercaptopropan-2-ols which proved to be of crucial importance for our purposes. Desulfurization failed in acetone solution, but by operating in ethyl methyl ketone solution and increasing the reaction time to 24 hours, essentially complete desulfurization could be accomplished, and cholestan-3β-ol (VIII), cholestan-3-one (IX) (over 80%) and *ca.* 52% of 1,1-diphenylpropan-2-ol (V) were isolated. The stability of this alcohol (V) toward these reduction conditions already has been mentioned above in the discussion of its derived mercaptoethanol IV. The resulting alcohol V, m.p. 58° was optically active ($[\alpha]^{25}D$ +5.8°; 3,5-dinitrobenzoate, $[\alpha]^{25}D$ −46.8°), but this did not prove whether this represented complete retention of configuration or partial racemization since the constants of optically pure 1,1-diphenylpropan-2-ol (V) are not known. However, as indicated above, the availability of three of the four possible diastereoisomers of the hemithioketal XXIII meant that at least one of them must belong to the enantiomeric series. Desulfurization of the third diastereoisomer of the hemithioketal XXIII proceeded in exactly the same manner to furnish 1,1-diphenylpropan-2-ol (V) of m.p. 58°, $[\alpha]^{25}D$ −5.8° (3,5-dinitrobenzoate, $[\alpha]^{25}D$ +44°). Since it is extremely unlikely that partial racemization in each instance should have occurred to exactly the same extent, one can conclude from the fact that the specific rotations of the pairs of alcohols V and of their 3,5-dinitrobenzoates were of the same magnitude but of opposite sign, that the desulfurization proceeded with retention of configuration of that carbon atom. This in turn implies that the oxygen in the alcohol V is that originally present in the hemithioketal XXIII and that only the C–O bond which is starred in XXIII has been broken.



XXIII

From the above results, we feel justified in concluding that the "normal" course of Raney nickel desulfurization of hemithioketals in acetone (or ethyl methyl ketone) solution involves the formation of predominantly (if not exclusively) oxygenated products, these being principally the original ketone and an alcohol, derived from the β-mercaptoethanol moiety.



(B)

Experiments to elucidate the intimate mechanism of this intriguing reaction and especially the source and mode of introduction of the "extra" oxygen atom are in process. We also are investigating the effects of certain structural variations in the hemithioketal molecule and of different desulfurization conditions upon the course of this reaction. Jaeger and Smith[14] just have reported that while Raney nickel desulfurization in acetone solution of the hemithioketals XXIV and XXV proceeds essentially by the above outlined scheme, the monohemithioketal XXVI of cyclohexane-1,2-dione leads to the ethyl ether XXVII. It may be appropriate to mention at this time that there is at least a third

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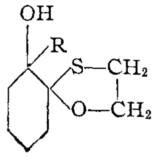
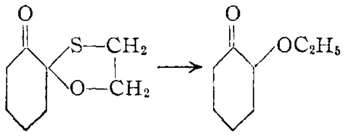
(13) (−)Phenylmethylcarbinol ($[\alpha]^{25}D$ −56.2° (*c* 1.3 in chloroform) $[\alpha]^{25}D$ −52.5° (*c* 1.7 in benzene)) was kindly provided by Prof. E. L. Eliel (University of Notre Dame) and was transformed into its 3,5-dinitrobenzoate (m.p. 121–122°, $[\alpha]^{25}D$ +41.2° (*c* 1.2 in chloroform)).

(14) R. H. Jaeger and H. Smith, *J. Chem. Soc.*, 160 (1955).

path open for the desulfurization of hemithioketals: employing an atmosphere of nitrogen in the total absence of water and oxygen-containing solvents, we have observed the production of a ketone and a hydrocarbon, the latter arising from the β-mercaptoethanol portion of the molecule.



XXIV, R = H
XXV, R = C_2H_5



XXVI XXVII

Experimental[15]

Desulfurization of 1,1-Diphenyl-3-mercaptopropan-2-ol (IV).—This represents a typical desulfurization procedure and only significant variations will be mentioned in subsequent desulfurizations.

W-2 Raney nickel catalyst[6] (5 g., 10 days old) was stirred for 1 hour in 100 cc. of refluxing methyl ethyl ketone followed by the addition of 0.5 g. of 1,1-diphenyl-3-mercaptopropan-2-ol (IV). After refluxing for 24 hours,[16] the solution was filtered, the filtrate evaporated to dryness and the residue was chromatographed in hexane solution on 15 g. of alumina. Elution with hexane furnished 102 mg. (24%) of 1,1-diphenylacetone (VI), m.p. 58–59° (after recrystallization from pentane), while from the hexane–benzene and benzene eluates there was isolated 240 mg. (55%) of 1,1-diphenylpropan-2-ol (V), m.p. 62–63°, undepressed upon admixture with an authentic sample prepared by lithium aluminum hydride reduction of VI.

The alcohol V and the ketone VI were treated under the same reaction conditions using the same solvent and catalyst on the same day as the above mercaptoethanol. In the case of the alcohol V, 92% of pure starting material was recovered after recrystallization from pentane. Infrared examination of the total crude product in the case of 1,1-diphenylacetone (VI) indicated the presence of a small amount of alcohol and the mixture was, therefore, treated with 3,5-dinitrobenzoyl chloride in pyridine solution. Approximately 7% of the 3,5-dinitrobenzoate of 1,1-diphenylpropan-2-ol (V) was obtained, m.p. 128°, not depressed on admixture with authentic material (m.p. 129–130°).

Desulfurization of 2β-Mercaptocholestan-3β-ol (VII).—Similar treatment of 150 mg. of 2β-mercaptocholestan-3β-ol[1] in acetone solution for 3 hours with 5-day old catalyst yielded 60 mg. of cholestan-3β-ol (VIII), m.p. 139–140°, and 20 mg. of cholestan-3-one (IX), m.p. 126–127°. Identification was confirmed in each instance by infrared comparison with authentic specimens. When 5-month old Raney nickel was employed the only difference noted was that a small amount of a poorly crystalline solid, m.p. 242–245°, was formed which may have been a bis-steroid. Desulfurization of VII in benzene solution, from which all ethanol adhering to the catalyst had been removed by azeotropic distillation, resulted in the formation of over 80% of cholestan-3-one (IX).

Both cholestan-3β-ol (VIII) and cholestan-3-one (IX) were recovered unchanged after refluxing with Raney nickel in either acetone or ethyl methyl ketone solution. However, when 0.28 g. of cholestan-3β-ol was refluxed in benzene solution (all ethanol removed by azeotropic distillation) with 2.8 g. of 7-month old Raney nickel, 0.21 g. of cholestan-3-one (m.p. 126–128°) was encountered. No particular study has been made of the age of the nickel catalyst upon this oxidation, but it appears that older samples are more effective.

In order to show that mercaptocholestanol (VII) indeed possessed the 3β-configuration,[7] 80 mg. of its diacetate (m.p. 106–108°, infrared acetate bands at 5.79 and 8.05 μ, thiolacetate band at 8.95 μ) was refluxed with 1 g. of W-4 Raney nickel[17] for 6 hours in 70 cc. of ethanol yielding 45 mg. of cholestan-3β-ol acetate, m.p. 105–107°.

***Desulfurization of 1,2-Diphenyl-2-mercaptoethanol* (X).**—Desulfurization of 150 mg. of X[1] in acetone solution (4 hours) with 30-day old Raney nickel followed by chromatography furnished (in the order in which they were eluted) 20 mg. of 1,2-diphenylethane (XIII), m.p. 49–50°, 28 mg. of desoxybenzoin (XII), m.p. 58–59°, and 42 mg. of 1,2-diphenylethanol (XI), m.p. 65–67°. All products were identified by direct comparison (mixture melting point and infrared spectra) with authentic samples. When the reaction was carried out with 6-month old Raney nickel in benzene (ethanol not removed), there was obtained 18 mg. of stilbene (XIV) (m.p. 122–124°), 20 mg. of desoxybenzoin (XII) and 46 mg. of 1,2-diphenylethanol (XI). The same products (12 mg. of XIV, 4 mg. of XII and 32 mg. of XI) were isolated when the reaction was carried out in acetone with 30-day old catalyst but reducing the time to 45 minutes. When ethanol was substituted for acetone, only 1,2-diphenylethane (XII) was formed.

Using the same 30-day old Raney nickel, refluxing for 5 hours in acetone transformed stilbene (XIV) into 1,2-diphenylethane (XIII), while 1,2-diphenylethanol (XI) gave a mixture consisting of starting material, desoxybenzoin (XII) and 1,2-diphenylethane (XIII). When ethanol was substituted for acetone in the last reaction, only 1,2-diphenylethane (XIII) was formed. No 1,2-diphenylethane was produced when the reaction time in the acetone run was reduced to 45 minutes, desoxybenzoin (12%) and starting material (XI) (80%) having been isolated.

Desulfurization of the Hemithioketal XV of Cyclohexanone and 2β-Mercaptocholestan-3β-ol.—The hemithioketal XV (0.2 g.) was desulfurized in the usual manner in acetone solution (5 hours) with 10-day old Raney nickel. The catalyst was filtered, the solvent was removed carefully from the filtrate on the steam-bath and 10 cc. of benzene was added and then distilled in order to remove any remaining acetone. To the residue was added water and the mixture was steam distilled until 20 cc. of distillate was obtained which was treated with 2 cc. of Brady reagent. The crude product was filtered and recrystallized from ethanol yielding 71 mg. (64%) of cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 157–159°, undepressed when mixed with authentic material. Ether extraction of the non-volatile portion followed by chromatography led to 32 mg. (21%) of cholestan-3-one (IX), m.p. 124–126°, and 93 mg. (60%) of cholestan-3β-ol (VIII), m.p. 138–140°.

Desulfurization of 2,3-Diphenyl-1-oxa-4-thiaspiro[4,5]-decane (XVI).—The desulfurization of 250 mg. of the hemithioketal XVI in acetone solution (2.5 hours) was carried out as in the preceding experiment, except that 4-day old Raney nickel was used. Steam distillation furnished 157 mg. (70%) of cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 157–159°, while chromatography of the non-volatile residue gave 10 mg. (7%) of stilbene (XIV), m.p. 122–124°, 17 mg. (11%) of desoxybenzoin (XII), m.p. 54–56°, and 68 mg. (42%) of 1,2-diphenylethanol (XI), m.p. 63–65°.

Desulfurization of Spiro-(4-phenyl-1,3-oxathiolane-2,3′-cholestane) (XVII).—The desulfurization of this hemithioketal (0.94 g.) also was carried out in acetone solution (45 minutes) with 2-week old Raney nickel catalyst. The steam distillate (*vide supra*) was saturated with sodium chloride and extracted with ether; the dried ether solution was divided into two portions and each was evaporated separately. One portion was heated for 15 minutes with 2 cc. of pyridine and 300 mg. of 3,5-dinitrobenzoyl chloride and then processed in the usual manner. Crystallization from hexane yielded 122 mg. (43% yield after multiplication by two) of the 3,5-dinitrobenzoate of β-phenethyl alcohol (XVIII), m.p. 105–107°, undepressed after mixing with an authentic specimen. No crystalline 2,4-dinitrophenylhydrazone could be obtained from the other portion.

The non-volatile residue was chromatographed and yielded first a gum ($\lambda_{max}^{CHCl_3}$ 5.83, 6.05, 6.78, 6.90 and 14.30 μ)

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[15] Melting points are uncorrected. Unless noted otherwise, rotations and infrared spectra (Baird double beam recording spectrophotometer using 0.1-mm. cells) were measured in chloroform solution. The microanalyses were carried out by Geller Laboratories, Hackensack, N. J.

[16] Essentially the same results were observed when the reaction was carried out for 5 hours in benzene solution from which the ethanol (under which the Raney nickel had been stored) was not removed. The only reason why the ethyl methyl ketone run was allowed to proceed for 24 hours was to duplicate as closely as possible the conditions required in the desulfurization of the hemithioketal XXIII.

[17] H. Adkins and A. A. Pavlic, THIS JOURNAL, **69**, 3039 (1947).

which may have contained some phenylacetaldehyde (XIX), while from the later eluates, 394 mg. (56%) of cholestan-3-one (IX) was isolated.

Desulfurization of Spiro-(5-phenyl-1,3-oxathiolane-2,3′-cholestane) (XX).—A sample (0.82 g.) of this hemithioketal was desulfurized on the same day and under exactly the same conditions as described for its isomer XVII. The steam distillate again was divided into two equal portions; one of them, after treatment with 2,4-dinitrophenylhydrazine, led to 27 mg. (12%) of acetophenone (XXI) 2,4-dinitrophenylhydrazone, m.p. 247–249°. The second portion was transformed into its 3,5-dinitrobenzoate yielding 87 mg. (35%) of phenylmethylcarbinol (XXII) 3,5-dinitrobenzoate, m.p. 94–95°, $[\alpha]^{25}\mathrm{D}$ +7° (*c* 0.9).[13] As pointed out in the discussion, this rotation could not be obtained reproducibly and in one run the product was found to be optically inactive. Chromatography of the non-volatile portion gave 0.409 g. (67%) of pure cholestan-3-one (IX).

Spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3′-cholestane) (XXIII).—A mixture of 10.0 g. each of cholestan-3-one (IX), 1,1-diphenyl-3-mercaptopropan-2-ol (IV), freshly fused zinc chloride and anhydrous sodium sulfate in 70 cc. of dioxane was shaken for 2 days and then allowed to stand at room temperature for an additional day. Dilution with ether, washing with water and 10% sodium carbonate solution, drying and evaporation left a residue which on successive concentration of its acetone solution gave three crystalline fractions (A, B and C).

Fraction A (4.1 g., m.p. 173–180°) was recrystallized several times from chloroform–methanol (2.93 g. (needles) to constant m.p. 193–194°, $[\alpha]^{28}\mathrm{D}$ +60°).

Anal. Calcd. for $C_{42}H_{60}OS$: C, 82.30; H, 9.87. Found: C, 82.04; H, 9.94.

Fraction B (3.3 g., m.p. 162–165°) was recrystallized three times from acetone; yield 1.67 g., m.p. 172–173° (needles), $[\alpha]^{25}\mathrm{D}$ −9.7°.

Anal. Calcd. for $C_{42}H_{60}OS$: C, 82.30; H, 9.87. Found: C, 82.15; H, 9.83.

Fraction C (3.6 g., m.p. 130–135°) crystallizes as prisms from acetone; yield 1.22 g., m.p. 70–80° then resolidifying and melting at 152–153°, $[\alpha]^{25}\mathrm{D}$ +2.8°.

Anal. Calcd. for $C_{42}H_{60}OS$: C, 82.30; H, 9.87. Found: C, 82.60; H, 10.17.

The infrared spectra (nujol mulls) of all three isomers showed distinct differences in the fingerprint region.

Desulfurization of Spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3′-cholestane) (XXIII).—W-2 Raney nickel catalyst (20 g., 3 days old) was refluxed with stirring for 1 hour with 250 cc. of ethyl methyl ketone, 2.0 g. of isomer A (m.p. 193–194°) of the hemithioketal XXIII was added and refluxing was continued with stirring for 24 hours. When the reaction was carried out in acetone solution, up to 80% of the hemithioketal was recovered.

The catalyst was filtered, the solvent was removed and the residue was chromatographed in 36 fractions over 30 g. of Merck acid-washed alumina. The first 23 fractions, eluted with petroleum ether, furnished 975 mg. (78%) of cholestan-3-one (IX), m.p. 126–127°, while from the petroleum ether–benzene (1:1) eluates, 20 mg. (2%) of cholestan-3β-ol (VIII), m.p. 138–139°, was obtained. The last 6 fractions, eluted with benzene, were combined and treated in pyridine solution with 3,5-dinitrobenzoyl chloride in the usual fashion. Crystallization from hexane gave 676 mg. (52%) of needles of the 3,5-dinitrobenzoate of (+)1,1-diphenylpropan-2-ol (V), m.p. 154.5–155°, $[\alpha]^{25}\mathrm{D}$ −46.1° (*c* 1.4), unchanged after three recrystallizations ($[\alpha]^{25}\mathrm{D}$ −46.8°).

Anal. Calcd. for $C_{22}H_{18}N_2O_6$: C, 65.02; H, 4.46. Found: C, 64.78; H, 4.36.

A sample (400 mg.) of the 3,5-dinitrobenzoate was refluxed for 2 hours with 300 cc. of 5% methanolic potassium hydroxide and the (+)1,1-diphenylpropan-2-ol was crystallized three times from pentane, the melting point changing only by 1°; prisms, m.p. 57.5–58°, $[\alpha]^{25}\mathrm{D}$ +5.8° (*c* 2.1).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.92; H, 7.64.

Desulfurization of 1.0 g. of isomer C (m.p. 152–153°) of the hemithioketal XXIII under precisely the same conditions yielded 80% of cholestan-3-one and 380 mg. (57%) of the 3,5-dinitrobenzoate of (−)1,1-diphenylpropan-2-ol (V), m.p. 154.5–155°, $[\alpha]^{25}\mathrm{D}$ +44° (*c* 1.7). Admixture with the above antipode lowered the m.p. to 129–130°, corresponding to the melting point of the racemic derivative which had been prepared independently.

Anal. Calcd. for $C_{22}H_{18}N_2O_6$: C, 65.02; H, 4.46. Found: C, 65.25; H, 4.57.

Saponification as described above followed by recrystallization from pentane yielded prisms of (−)1,1-diphenylpropan-2-ol, m.p. 57.5–58°, $[\alpha]^{25}\mathrm{D}$ −5.8° (*c* 2.6).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.56; H, 7.63.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds. XV. Biradical Sources. The Synthesis and Decomposition of Large Membered Ring Azo Compounds[1]

BY C. G. OVERBERGER AND MILTON LAPKIN[2]

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The cyclic bis azo compounds VI (n = 8,10) have been prepared and characterized. A study of the decomposition of VI, n = 8, in xylene at 120° resulted in the isolation and characterization of VII, a twenty-membered carbon ring. From the rate data obtained, it is suggested that both azo linkages in VI, n = 8, do not decompose at exactly the same rate. Decomposition of VI, n = 8, in styrene gave no polystyrene under conditions in which a similar radical derived from a linear azo compound produced polymer. Thus, it is clear that biradical propagation cannot take place even under these favorable conditions.

We have initiated a study of the properties of moderately active biradicals in solution. A principal difficulty encountered in such a study has been the availability of biradical sources. There are numerous examples in the literature of organic compounds which are reported to contain two unpaired electrons in the triplet state. For the most part, however, these are either of the very stable triphenylmethyl type or very unstable biradicals suggested as intermediates in gas phase decompositions. It is impossible in an article of this type to review adequately the background but a compilation of references seems pertinent. One of the first compounds reported which showed some

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[1] Presented in part before the Polymer Division at the 126th Meeting of the American Chemical Society, New York, September 12–17, 1954. This is the 15th in a series of papers concerned with the preparation and decomposition of azo compounds. For the 14th paper in this series, see C. G. Overberger and B. F. Marks, THIS JOURNAL, **77**, 4104 (1955).

[2] This paper comprises a portion of a thesis presented by Mr. M. Lapkin in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.