of water, 10% sodium thiosulfate, water, concd. sulfuric acid, water, 10% sodium bicarbonate, water and dried over anhydróus magnesium sulfate. The pentane was removed at reduced pressure through a 20-cm. Vigreux column and the remaining product was distilled at 10 mm. in a micro distillation apparatus yielding 0.75 g. of 4-methylcyclohexyl bromide (80%). Infrared analysis of the product indicated that it contained 9% cis- and 91% trans-4-methylcyclohexyl bromides.

Cleavage by Pyridinium Bromide Perbromide in Acetic Acid.—A mixture of 1.9 g. (0.0060 mole) of pyridinium bromide perbromide and 2 g. (0.0053 mole) of trans-4-methylcyclohexylmercuric bromide was dissolved in 25 ml. of glacial acetic acid. The solution was stirred for 2.5 hr. at 25° and the product was worked up as described for the bromine cleavage in acetic acid to yield 0.70 g. of 4-methylcyclohexyl bromide (74%). Infrared analysis of the product indicated that it contained greater than 99% trans-4-methylcyclohexyl bromide.

Cleavage by N,N-Dibromobenzenesulfonamide in Acetic Acid.—The experimental procedure was the same as described for the pyridinium bromide perbromide cleavage in acetic acid.

Cleavage by Bromine and Zinc Bromide in Acetic Acid.—The experimental procedure was the same as described for the bromine cleavage in acetic acid with the exception that a molar amount of zinc bromide was added to the reaction flask.

Cleavage by Hypobromous Acid in 50% Dioxane-50% Water.—To a solution of 2 g. (0.0053 mole) of cis-4-methylcyclohexylmercuric bromide in 70 ml. of dioxane was added a solution of 0.078 M hypobromous acid (the hypobromous acid was prepared by stirring a mixture of mercuric oxide, bromine and water together, distilling at reduced pressure and washing the distillate with carbon tetrachloride) and 0.40 ml. of concd. sulfuric acid, over a period of one hour at 25°. The entire reaction was carried out under a nitrogen atmosphere in the dark. After stirring for 2 hr., a sample was titrated with standard sodium thiosulfate solution and the reaction was found to be 90% complete. The solution was filtered and 50 ml. of pentane was added. The pentane layer was separated and washed successively with water, concd. sulfuric acid, water, 5% sodium bicarbonate, water and dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure and the product was distilled at 10 mm. in a micro distillation apparatus to yield

0.26 g. of 4-methylcyclohexyl bromide (28%). Infrared analysis of the product indicated that it contained 46% cis- and 54% trans-4-methylcyclohexyl bromides.

Cleavage by Bromine in Pyridine.—In a 300-ml., 3-necked round-bottom flask fitted with a Teflon mechanical stirrer and a 60-ml. dropping funnel was placed 30 g. (0.079 mole) of trans-4-methylcyclohexylmercuric bromide and 150 ml. of pyridine. (The pyridine was purified by distilling from toluenesulfonyl chloride through a 30-plate column.) In the dropping funnel was placed 13.0 g. (0.081 mole) of anhydrous bromine in 25 ml. of pyridine. The bromine solution was added slowly over a period of 0.5 hr. at 25°. The reactants were stirred at 25° for 1 hr. and poured into a 1-l. beaker containing 150 ml. of hexane. Approximately 300 ml. of water was added and the resulting mercuric bromide precipitate was removed by filtration with suction. The hexane layer was removed and the remaining pyridine–water layer was reëxtracted with hexane. The combined hexane layers were washed successively with water, concd. sulfuric acid, water, 5% sodium bicarbonate, water and dried over anhydrous magnesium sulfate. The hexane was removed by distilling at reduced pressure through a 15″ tantalum spiral wire column. The remaining product was distilled to yield 9.3 g. of trans-4-methylcyclohexyl bromide (66%), b.p. 57.0° (9.5 mm.), m.p. 25.0–26.0°, $n^{29.9}$D 1.4800; characteristic infrared maxima (carbon disulfide): 7.50(m), 8.89(m), 9.30(w), 9.95(m), 10.35(s), 11.33(w), 11.63(s), 12.75(m) and 14.20(s) μ.

Similarly, 12 g. (0.0318 mole) of cis-4-methylcyclohexylmercuric bromide was cleaved by bromine in pyridine at 0° yielding 3.1 g. of cis-4-methylcyclohexyl bromide (55%), b.p. 57.0–57.8° (9.5 mm.), $n^{29.9}$D 1.4843; characteristic infrared maxima (carbon disulfide): 7.41(m), 7.67(m), 9.06-(m), 9.75(m), 10.32(w), 10.40(m), 10.57(m), 11.46(w), 11.80(m), 14.13(w) and 14.60(s) μ.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40; Br, 45.13. Found for trans-$C_7H_{13}Br$: C, 47.53; H, 7.58; Br, 44.88. Found for cis-$C_7H_{13}Br$: C, 47.30; H, 7.52; Br, 45.09.

Within the sensitivity of our methods for detecting each isomer (infrared, less than 1%), the cis- and trans-4-methylcyclohexyl bromides are homogeneous.

BERKELEY, CALIF.

Conformation of 3α-Phenyl-3β-tropanyl Phenyl Ketone; a Novel Nitrogen–Carbonyl Interaction

BY M. R. BELL AND S. ARCHER

The abnormal spectral behavior of 3α-phenyl-3β-tropanyl phenyl ketone (IIa) is interpreted as evidence that the piperidine ring exists in the boat conformation with resultant nitrogen–carbonyl interaction. The normal spectral behavior of appropriate model compounds indicated that IIa adopts this conformation to relieve the non-bonded interaction between the 3α-phenyl group and the ethylene bridge.

During synthetic studies directed toward the preparation of 3α-phenyl-3β-tropanecarboxylic acid we prepared 3α-phenyl-3β-tropanyl phenyl ketone (IIa) by a route analogous to that used for the corresponding piperidine derivative (IV).[1] The starting material, α-ecgonine methyl ester (Ia), has long been known[2] but only recently been assigned the correct stereochemical structure on the basis of chemical and spectral evidence.[3] Before Heusner's observations were available we had relied on the observation of intramolecular hydrogen bonding

in the infrared spectrum to arrive at the same formulation.

Reaction of the α-ecgonine ester with phenyllithium afforded 3α-diphenylhydroxymethyl-3β-tropanol (Ib) which was transformed by zinc chloride in acetic anhydride to a crystalline base whose analysis and those of its derivatives were in accord with the values expected for the ketone IIa. Reduction either catalytically or with lithium aluminum hydride furnished the alcohol IIIa which could be oxidized to the parent ketone with chromic acid in acetic acid; IIa formed an oxime but only under forcing conditions indicating the relatively unreactive condition of the carbonyl group. Other trans-

(1) R. E. Lyle and G. G. Lyle, THIS JOURNAL, 76, 3536 (1954).

(2) R. Willstätter, Ber., 29, 2216 (1896).

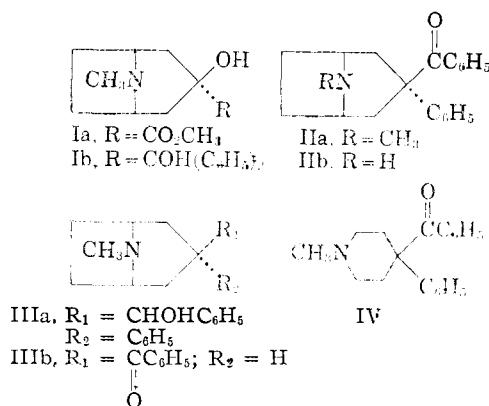(3) A. Heusner, Z. Naturforsch., 126, 602 (1957).

TABLE I[6]

ULTRAVIOLET AND INFRARED SPECTRAL DATA[a]

| Compound | Ultraviolet | | Infrared, μ (6μ region)[b] | |
	Base	Hydrochloride	Base	Hydrochloride
IIa	Genl. strong abs.[c] (see Fig. 1)	252(1000)	No. abs. below 6.25	6.00(weak)
IIa methobromide	248(9640) 317(353)		5.97(strong)	
IIb	258(420)	258(564)	No abs. below 6.25; hydroxyl at 2.84[d]	No abs. below 6.35
IIIa	259(384)	.....	....	....
IIIb	242(11,300) 315(117)	243(12,900) 310(infl., 108)	5.97(strong)	5.97(strong)
IV	244(9720)	247(10,400) 320(251)	5.98(strong)	5.96(strong)
IIa[e]	Genl. strong abs. (see Fig. 1)	.....	6.02(strong)	....
IV[e]	242(10,300) 321(252)	.....	5.96(strong)	....

[a] Wave lengths are those of the maxima in $m\mu$ unless otherwise indicated. The numbers in parentheses are the corresponding extinction coefficients. The solvent is methanol unless otherwise indicated. [b] The infrared spectra in methanol were determined using a 0.0245-mm. silver chloride cell. [c] Unaffected by addition of alkali which indicates that the spectrum is not the result of reaction with carbon dioxide. [d] In bromoform. [e] In methylene chloride.

formations of IIa which establish the precise structure as written will be described in a subsequent publication.[4] The present report is concerned with the interpretation of the unusual spectral behavior of this ketone.

Ia, R = CO₂CH₃
Ib, R = COH(C₆H₅)₂   IIa, R = CH₃
                             IIb, R = H

IIIa, R₁ = CHOHC₆H₅   IV
      R₂ = C₆H₅
IIIb, R₁ = CC₆H₅; R₂ = H
         ‖
         O

3α-Phenyl-3β-nortropanyl phenyl ketone (IIb) was prepared by von Braun demethylation of IIa followed by acid hydrolysis of the intermediate cyanamide. The model compound 3β-tropanyl phenyl ketone (IIIb) was synthesized from 3β-tropanyl nitrile by reaction with phenyllithium. This ketone was identical with that prepared from the 3α-nitrile with phenylmagnesium bromide.[5] In the latter preparation epimerization had occurred either during the Grignard reaction or during the subsequent acid hydrolysis of the intermediate iminoketone to give the more stable 3β-tropanyl ketone.

Both the ultraviolet and infrared spectra (Table I and Figs. 1 and 2) were obtained in methanol to ensure that the same species was under observation in each determination although, of course, there are vast concentration differences. Methanol was the only solvent found in which both the hydrochlorides and bases were soluble and which was sufficiently transparent in the 6μ and ultraviolet regions to be of use.

The models IIIb and IV in the form of the base and hydrochloride exhibit the spectral absorption characteristic of an alkyl phenyl ketone as does the methobromide of IIa.

The abnormal spectral behavior of IIa in the ultraviolet in both methylene chloride and methanol is characterized by the lack of peak absorption in the 240–250 and 320 mμ regions and by a decreased intensity of absorption in the 240–250 mμ area. There is a significant decrease in absorption intensity when the solvent is changed from methylene chloride to methanol. In contrast, the absorption of the model piperidine analog IV is virtually unaffected by this solvent change. The infrared spectrum of IIa in methanol shows virtually no absorption in the 6 μ region while in methylene chloride there is a carbonyl peak at 6.02 μ. The piperidine analog IV absorbs at 5.96 μ in both solvents.

It is possible but highly unlikely that the behavior of IIa in methanol is the result of hemiketal formation since it has been shown recently that hindered ketones do not add methanol with any degree of facility.[7] If hemiketalization were significant it is difficult to see why IIIb and IV would escape this reaction while IIa succumbs. Furthermore, the hemiketal from IIa should have the same ultraviolet spectrum as IIIa and a mixture of hemiketal and ketone would have intermediate absorption. This is clearly not the case.

We suggest that the unusual spectral behavior is caused by the existence of IIa in the boat conformation with resultant nitrogen–carbonyl interaction as depicted in V. Since both IIIb and IV show normal spectral behavior the 3α-phenyl group and the ethylene bridge are necessary structural features for retention of the piperidine ring of IIa in the boat form. The driving force is the relief of 1,3-diaxial interaction between the ethylene bridge and the 3α-phenyl group when the piperidine ring is in the usually more stable chair conformation.

Nitrogen–carbonyl interactions occur in compounds wherein the nitrogen and carbonyl groups

(4) M. R. Bell and S. Archer, to be published.
(5) S. Archer, et al., THIS JOURNAL, 80, 4677 (1958).
(6) We are greatly indebted to Dr. Frederick C. Nachod and his staff for determination of the spectra.
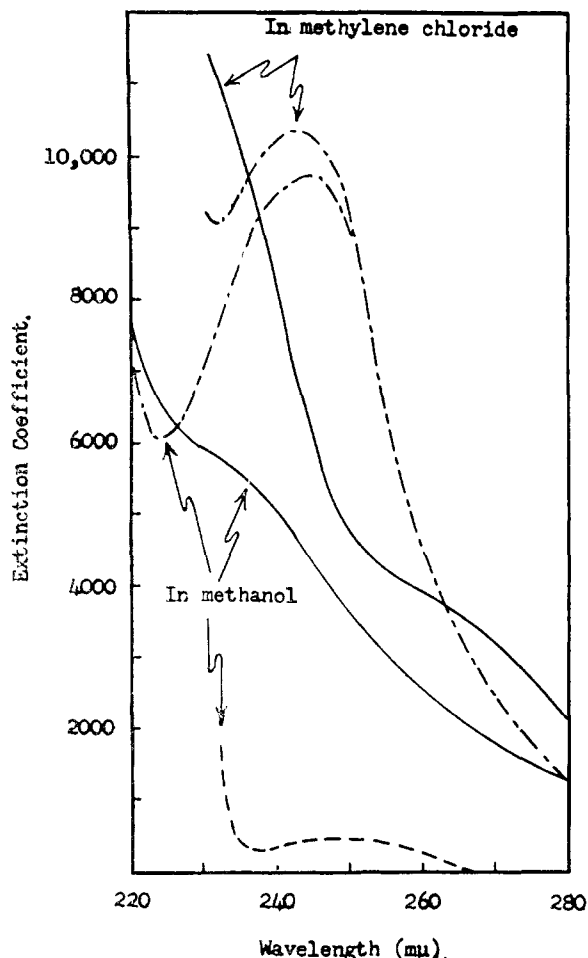(7) C. Djerassi, L. A. Mitscher and B. J. Mitscher, ibid., 81, 947 (1959).

Fig. 1.—Ultraviolet spectra of IIa (————), IIb (– – – –) and
IV (——— -) in methanol and methylene chloride.

Fig. 2.—Ultraviolet spectra of the hydrochlorides of IIa
(————), IIb (– — – –) and IV (——— -) in methanol.

are part of one ring although Leonard has cited a case in which this phenomenon occurs in an acyclic system.[8] As far as we are aware IIa is the first example in which the nitrogen is cyclic and the carbonyl group is acyclic.

The fact that general ultraviolet absorption is still present is in harmony with the concept of interacted rather than completely reacted nitrogen and carbonyl functions. Leonard's aminoketones which display nitrogen–carbonyl interaction show new absorption in the 230 mμ region.[9] We did not observe new peaks in this area but there is general rising absorption (Fig. 1) which is probably the result of phenyl conjugation with the new chromophore. The shift of the infrared carbonyl absorption peak to longer wave lengths in going from IV (non-interacted) to IIa is characteristic of interacted aminoketones.[8]

The effect of solvent change on the spectral behavior of the N---C === O chromophore does not appear to have been observed before. We suggest that the behavior of IIa in methanol is the result of a greater degree of nitrogen–carbonyl interaction in this solvent than in methylene chloride. It seems

reasonable to assume that methanol would be better able to stabilize by some appropriate solvation mechanism the partial charge separation which is produced by the interaction.

The "nor" ketone IIb and its hydrochloride show no carbonyl absorption in the infrared and only weak absorption in the ultraviolet, the latter resembling closely that of IIIa. The infrared spectrum of IIb in bromoform exhibits hydroxyl absorption at 2.84 μ. Therefore, IIb exists in the completely reacted form as the carbinolamine VII.

(8) For a review of transannular nitrogen–carbonyl interactions by an outstanding contributor to this field see N. J. Leonard in *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **17**, 243 (1956).

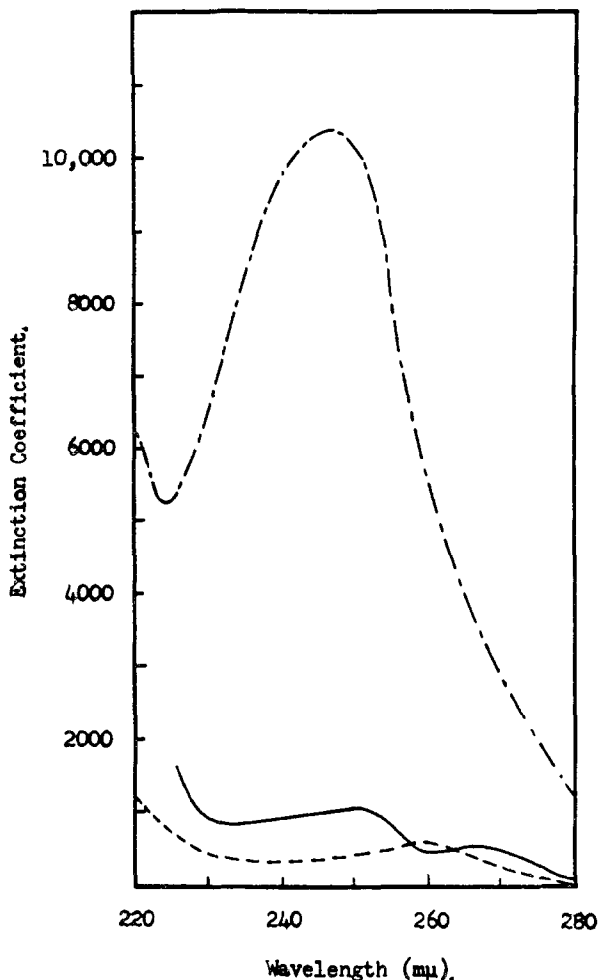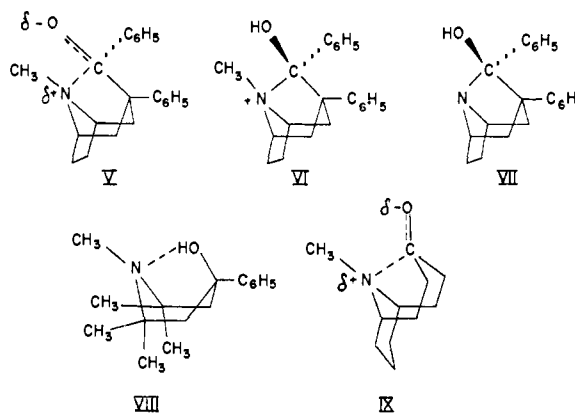(9) N. J. Leonard and M. Oki, This Journal, **77**, 6239 (1955).

The hydrochloride of IIa in methanol is probably a mixture consisting mainly of the form with completely reacted nitrogen and carbonyl function as in VI in equilibrium with the form possessing a normal ketone function since the ultraviolet spectrum resembles that of VII but, in addition, shows a weak phenyl ketone band (Fig. 2); the infrared spectrum displays a weak band at 6.00 μ.

Since the completion of our work two opposite cases of nitrogen interactions have appeared. Lyle[10] reported that the piperidinol VIII exhibited intra-molecular hydrogen bonding, but that the piperidinol lacking the *gem*-dimethyl groups did not. Leonard[11] showed that the bicyclic ketone IX exists in the conformation which allows strong interaction between the amine and carbonyl functions.

Experimental[12]

3α-Diphenylhydroxymethyl-3β-tropanol (Ib).—A solution of 100 g. of α-ecgonine methyl ester[2] in 325 ml. of tetrahydrofuran was added during 20 minutes to a stirred solution of phenyllithium (prepared from 316 g. of bromobenzene and 27.9 g. of lithium wire) in one liter of ether. The reaction mixture was refluxed for 1 hr., cooled and decomposed with 300 ml. of water. The solid precipitate was filtered off, washed with ether and the combined filtrates charcoaled and dried over anhydrous sodium sulfate. Addition of alcoholic hydrogen chloride gave directly 167 g. of the hydrochloride as a white crystalline powder which melted at 278–280° dec. The analytical sample melted at 280–281° dec. after two recrystallizations from methanol–ether.

Anal. Calcd. for $C_{21}H_{26}ClNO_2$: C, 70.08; H, 7.28; Cl, 9.85. Found: C, 69.99; H, 7.39; Cl, 9.74.

A sample of the free base, generated from the hydrochloride with aqueous sodium carbonate, melted at 116–117° after three recrystallizations from hexane.

Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33. Found: C, 77.93; H, 7.85; N, 4.29.

3α-Phenyl-3β-tropanyl Phenyl Ketone (IIa).—A stirred suspension of 98 g. of 3α-diphenylhydroxymethyl-3β-tropanol hydrochloride in 250 ml. of acetic anhydride was treated in one portion with 98 g. of fused, powdered zinc chloride. The reaction flask was immersed in an ice-bath to moderate the initially mildly exothermic reaction. After stirring for one hour, the clear dark brown solution was left at room temperature for 63 hours and then poured into a solution of 250 g. of sodium hydroxide in 2 liters of water. The solid which separated was collected by filtration and extracted with 1 liter of methylene chloride. Evaporation of the combined, dried extracts and crystallization of the residual oil from 600 ml. of hexane gave 48.5 g. of light brown needles, m.p. 117–122.5°. Recrystallization from 700 ml. of boiling hexane afforded 38.7 g. of white nuggets, m.p. 121–122.5°.

Anal. Calcd. for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.87; H, 7.43; N, 4.57.

The hydrochloride melted at 257–257.5° dec. after recrystallization from absolute alcohol.

Anal. Calcd. for $C_{21}H_{24}ClNO$: C, 73.77; H, 7.08; Cl, 10.37. Found: C, 73.50; H, 6.98; Cl, 10.13.

The methobromide was prepared from the free base and methyl bromide in acetone; m.p. 256–258.5° after recrystallization from methanol–ether.

Anal. Calcd. for $C_{22}H_{26}BrNO$: Br, 19.96. Found: Br, 19.86.

The oxime was prepared by refluxing 10 g. of the ketone and 10 g. of hydroxylamine hydrochloride in 25 ml. of pyridine and 75 ml. of absolute alcohol for 15 hours.[13] During this period the very insoluble oxime hydrochloride separated directly from the hot solution. The white, microcrystalline

solid was filtered off, washed with alcohol and water and dried; weight 11.0 g., m.p. 327° dec.

Anal. Calcd. for $C_{21}H_{25}ClN_2O$: C, 70.67; H, 7.06; N, 7.85. Found: C, 70.52; H, 6.86; N, 7.72.

3α-Phenyl-3β-tropanylphenylcarbinol (IIIa)-Lithium Aluminum Hydride Reduction of IIa.—To a warm stirred suspension of 0.5 g. of lithium aluminum hydride in 100 ml. of ether was added a solution of 2.0 g. of 3α-phenyl-3β-tropanyl phenyl ketone in 100 ml. of ether. The mixture was refluxed for 6 hours, cooled and decomposed by addition of 1 ml. of water followed by 1 ml. of 35% sodium hydroxide. The solid which separated was filtered off and extracted with boiling chloroform. Evaporation of the combined, dried extracts left 2.1 g. of a white, crystalline solid, m.p. 150–160°, which melted at 162–163° after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{21}H_{25}NO$: C, 82.01; H, 8.20; N, 4.56. Found: C, 82.36; H, 8.55; N, 4.52.

Catalytic Hydrogenation of IIa.—A solution of 3.06 g. of 3α-phenyl-3β-tropanyl phenyl ketone in 225 ml. of grain alcohol was shaken with 0.20 g. of platinum oxide and hydrogen at 46 p.s.i. for 1.5 hours. The hydrogen absorption amounted to 96% of theoretical. The catalyst was filtered off and the filtrate evaporated to dryness under reduced pressure. The white crystalline residue was recrystallized from benzene–hexane to give 2.5 g. of fine, white needles, m.p. 162–163°. A second recrystallization gave needles, m.p. 162.5–164°, undepressed on admixture with the alcohol formed by lithium aluminum hydride reduction of IIa.

Oxidation of 3α-Phenyl-3β-tropanylphenylcarbinol.[14]—To a warm (60–70°) solution of 2 g. of 3α-phenyl-3β-tropanylphenylcarbinol (m.p. 162.5–164°) in 30 ml. of acetic acid was added slowly with stirring a solution of 0.43 g. of chromic acid in 1 ml. of water and 10 ml. of acetic acid during a period of 2 hours. After being stirred at 65° for 1.5 hours and 100° for 2 minutes, the mixture was cooled, poured into excess sodium hydroxide and extracted five times with 100-ml. portions of ether. The ether was evaporated *in vacuo* on the steam-bath. The residue was dissolved in methylene chloride, dried over anhydrous sodium sulfate, charcoaled and evaporated to give an oil. This was dissolved in boiling hexane and cooled to give 0.7 g. of a white solid, m.p. 158–170°, which consisted mostly of starting alcohol. The filtrate was concentrated to a few milliters and yielded 0.4 g. of white crystals, m.p. 118.5–123° (mostly 121.5–123°), which was shown by mixed melting point comparison to be identical with IIa.

8-Cyano-3α-phenyl-3β-nortropanyl Phenyl Ketone.—To a stirred solution of 7.1 g. of distilled cyanogen bromide in 100 ml. of benzene at 50–55° was added during 3 hours a solution of 10.0 g. of 3α-phenyl-3β-tropanyl phenyl ketone in 250 ml. of benzene. Stirring and warming at 50–55° were continued for 2 hours. The mixture was left at room temperature for 15 hours, filtered and evaporated to dryness. The white, crystalline residue was recrystallized from methanol to give 4.3 g., m.p. 156–159°, and 1.4 g., m.p. 157–160°. Recrystallization of the combined crops from methanol gave white needles, m.p. 161–162°.

Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.71; H, 6.37; N, 8.86. Found: C, 79.66; H, 6.33; N, 8.67.

3α-Phenyl-3β-nortropanyl Phenyl Ketone (IIb).—A mixture of 1.0 g. of 8-cyano-3α-phenyl-3β-nortropanyl phenyl ketone and 50 ml. of concentrated hydrochloric acid was refluxed for 7 hours, evaporated to two-thirds the original volume under reduced pressure and made basic by addition of excess solid potassium carbonate. The oil which separated was extracted with methylene chloride. Evaporation of the dried extracts and recrystallization of the solid residue from acetone yielded 0.41 g. of small, white crystals, m.p. 198–207°. Two recrystallizations from absolute alcohol afforded thick, white needles, m.p. 208–212°.

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.27; N, 4.81. Found: C, 82.56; N, 6.94; N, 4.78.

The hydrochloride, after recrystallization from 1-propanol–ether, melted at 297° dec.

Anal. Calcd. for $C_{20}H_{22}ClNO$: C, 73.27; H, 6.77; Cl, 10.82. Found: C, 73.38; H, 6.66; Cl, 10.84.

3β-Tropanyl Phenyl Ketone (IIIb).—A solution of 1.0 g. of 3β-tropanylnitrile[5] in 30 ml. of ether was added to 50 ml

(10) R. E. Lyle, *J. Org. Chem.*, **22**, 1280 (1957).

(11) N. J. Leonard, D. F. Morrow and M. T. Rogers, THIS JOURNAL, **79**, 5476 (1957).

(12) We are indebted to Mr. Morris E. Auerbach and his staff for the analytical determinations.

(13) W. Bachmann and M. Barton, *J. Org. Chem.*, **3**, 300 (1939).

(14) R. Willstätter, *Ber.*, **29**, 393 (1896).

of ethereal phenyllithium (prepared from 2.1 ml. of bromo-benzene and 0.35 g. of lithium wire). Gentle reflux ensued which was maintained by heating for 2 hours. After addition of 50 ml. of dilute hydrochloric acid and evaporation of the ether the aqueous residue was warmed on the steam-bath for 1 hour. The solution was made strongly basic by addition of 35% sodium hydroxide and extracted with ether. Addition of alcoholic hydrogen chloride to the dried extracts precipitated the hydrochloride as a gum which crystallized under acetone to give 0.96 g. of white crystals, m.p. 234–

236°. Recrystallization from boiling propyl alcohol raised the melting point to 241–242°.

Anal. Calcd. for $C_{15}H_{20}ClNO$: C, 67.78; H, 7.59; Cl, 13.34. Found: C, 68.10; H, 7.69; Cl, 13.32.

A mixed melting point comparison of this product with that prepared from 3α-tropanyl nitrile and phenylmagnesium bromide[6] resulted in a slight depression, but their infrared spectra were identical.

RENSSELAER, N. Y.

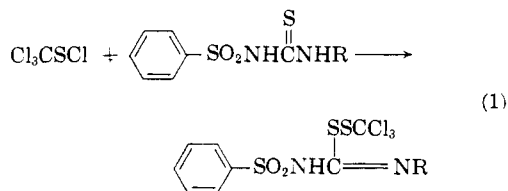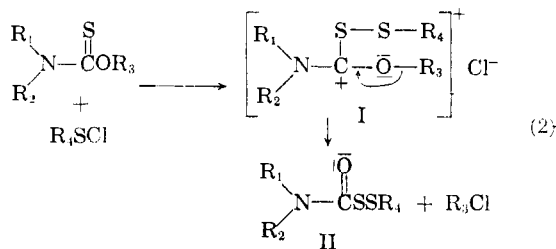# The Reactions of Sulfenyl Chlorides with Thionocarbamates

BY JOHN F. HARRIS, JR.

The reaction of sulfenyl chlorides with thionocarbamates has been found to yield alkyl or aryl carbamoyl disulfides. When the reaction is carried out in the presence of base, (dithio)-formimidic esters are obtained.

The sulfenyl halides, RSX, constitute a class of compounds well known for their high degree of reactivity with many types of molecules,[1] *e.g.*, olefins, acetylenes,[2] thiols, amines, ketones and compounds containing activated aromatic nuclei. However, little has been known concerning their reactions with compounds containing the thiocarbonyl group. Recently, one such reaction involving arylsulfonyl thioureas was reported[3]

$$Cl_3CSCl + \underset{}{\text{C}_6\text{H}_4}\text{—SO}_2\text{NH}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{NHR} \longrightarrow$$

$$\text{C}_6\text{H}_4\text{—SO}_2\text{NH}\overset{\text{SSCCl}_3}{\underset{}{\text{C}}}\text{=NR} \quad (1)$$
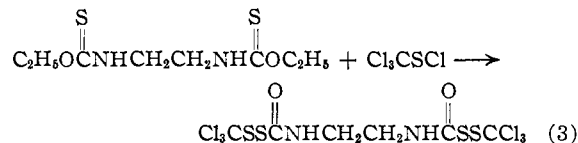
It has now been found that sulfenyl chlorides react readily with another class of thiocarbonyl compounds, the esters of thionocarbamic acids. The products normally obtained are unsymmetrical carbamoyl disulfides. The reaction is conveniently represented by the sequence

$$\begin{array}{c} \text{R}_1 \\ \diagdown \\ \text{N—COR}_3 \\ \diagup \quad \overset{\text{S}}{\overset{\|}{}} \\ \text{R}_2 \\ + \\ \text{R}_4\text{SCl} \end{array} \longrightarrow \left[\begin{array}{c} \text{R}_1 \quad \text{S—S—R}_4 \\ \diagdown \quad | \\ \text{N—C}\!-\!\overset{+}{\text{O}}\!-\!\text{R}_3 \\ \diagup \\ \text{R}_2 \quad \quad \text{I} \end{array} \right]^+ \text{Cl}^- $$

$$\downarrow$$

$$\begin{array}{c} \text{R}_1 \quad \overset{\text{O}}{\overset{\|}{}} \\ \diagdown \\ \text{N—CSSR}_4 + \text{R}_3\text{Cl} \\ \diagup \\ \text{R}_2 \quad \text{II} \end{array} \quad (2)$$

In this scheme the R_4S^+ ion attacks the thionocarbamate at the relatively negative sulfur atom to form the intermediate I. This intermediate expels the alkyl group on the oxygen to produce a carbamoyl disulfide II and an alkyl chloride. The reactions are carried out by mixing equimolar amounts of the reactants in an inert solvent, such

as ether or benzene, and allowing the mixture to stand at room temperature for an hour or so. Evaporation of the solvent at room temperature leaves the product in high yield.
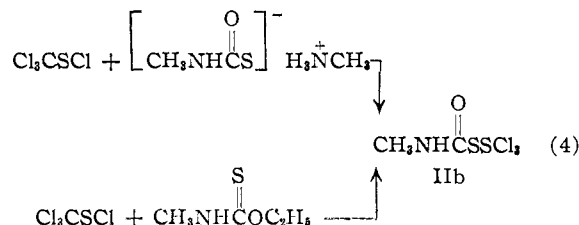
The reaction appears to be general and constitutes a convenient route to carbamoyl disulfides of the general type II. Compounds where R_1 and R_2 = H, alkyl, aryl and R_4 = Cl_3C, C_2H_5, $p\text{-ClC}_6H_4$, $o\text{-NO}_2C_6H_4$, have been prepared. The reaction was also successful with a bis-thionocarbamate

$$\text{C}_2\text{H}_5\text{O}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{NHCH}_2\text{CH}_2\text{NH}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{OC}_2\text{H}_5 + \text{Cl}_3\text{CSCl} \longrightarrow$$

$$\text{Cl}_3\text{CSS}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NHCH}_2\text{CH}_2\text{NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{SSCCl}_3 \quad (3)$$

The yields of II are generally better than 70%. In one case, the alkyl chloride was isolated in 73% yield. No compounds represented by II appear to have been described previously. The properties of the examples prepared in this work are recorded in Table I.

The structures of the carbamoyl disulfides II were established by elemental analysis and infared spectroscopy. As expected, the spectra of these compounds exhibit typical amide absorption frequencies (Table II).

Further confirmation of structure II was obtained by the synthesis of trichloromethyl N-methylcarbamoyl disulfide (IIb) by the reaction of trichloromethanesulfenyl chloride and methylammonium N-1. ethylthiocarbamate. This product proved to be identical with the product obtained from the reaction of trichloromethanesulfenyl chloride with N-methylthionocarbamate

$$Cl_3CSCl + \left[\text{CH}_3\text{NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{S} \right]^- \text{H}_3\overset{+}{\text{N}}\text{CH}_3$$

$$\downarrow$$

$$\text{CH}_3\text{NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{SSCl}_3 \quad (4)$$

$$\quad \text{IIb} \quad \uparrow$$

$$Cl_3CSCl + \text{CH}_3\text{NH}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{OC}_2\text{H}_5 \underrightarrow{\qquad}$$

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(3) A. Margot and H. Gysin, U. S. Patent 2,813,902 (1957).