Two maxima are found in the ultraviolet spectrum: 264 mμ (log ε 4.74) and 308 mμ (log ε 4.19). The infrared spectrum exhibits *p*-disubstituted benzene absorption bands at 824 and 811 cm.$^{-1}$. Other aromatic bands occur at 798, 762, 757 and 748 cm.$^{-1}$. Absorption associated with the methyl group is found at 2905, 2845, 1386 and 1376 cm.$^{-1}$, but no functional group absorption is present.

The second solid isolated from the chromatographic separation was crystallized twice from ethanol–benzene; yield 0.43 g. (11%), m.p. 256–259°. Two additional crystallizations furnished an analytical sample of 9,10,10-tri-*p*-tolyl-9,10-dihydro-9-phenanthrol, m.p. 260–261°.

Anal. Calcd. for $C_{35}H_{30}O$: C, 90.09; H, 6.48. Found: C, 90.08; H, 6.77.

The infrared spectrum contains absorption assigned to a tertiary alcohol (3560, 1334, 1173, 1159 cm.$^{-1}$). The spectrum is very similar to that of the phenanthrol III except for bands attributable to the methyl groups.

Treatment of 10,10-Diphenyl-9,10-dihydro-9-phenanthrone with *t*-Butylmagnesium Chloride at 110°.—To the Grignard reagent prepared from 10.0 ml. (0.092 mole) of *t*-butyl chloride, 2.00 g. (0.083 g. atom) of magnesium and 50 ml. of ether was added a suspension of 3.46 g. (0.0100 mole) of the phenanthrone II in 40 ml. of anisole. The temperature of the mixture was adjusted to 110° and the volume to 80 ml. by distillation of the ether and addition of anisole. The green reaction mixture was heated at 110° for 24 hr. A stream of dry air then was passed over the hot mixture for 0.5 hr.; this reduced the volume in the reaction flask to 40 ml. A saturated ammonium chloride solution was introduced into the flask to effect hydrolysis. Following the addition of benzene to this mixture, the organic layer was removed, dried over sodium carbonate and concentrated. The infrared analysis of the red-brown semisolid residue (4.92 g.) indicated that less than 10% of any ketonic material was present. Treatment of this residue with 15 ml. of ethanol caused separation of a white solid (1.62 g., m.p. 233–239°) from the red oil. After crystallization from ethanol–benzene, the compound melted at 238–243°, yield 1.40 g. (36%). An analytical sample of the 3-*t*-butyl-9,10-diphenylphenanthrene (XIV) in the form of fine needles, m.p. 242–243°, was obtained by two additional crystallizations.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.63; H, 6.86.

The infrared spectrum exhibits no absorption assignable to a functional group. Absorption characteristic of the *t*-butyl group occurs at 2950, 1407 and 1358 cm.$^{-1}$. Absorption assignable to a 1,2,4-trisubstituted benzene ring is found at 878 cm.$^{-1}$ (weak) and 829 cm.$^{-1}$ (strong). In addition, bands associated with *o*-disubstituted and monosubstituted benzene rings are present. Two maxima appear in the ultraviolet spectrum: 260 and 305 mμ, for which the log ε values are 4.82 and 4.17, respectively.

When this Grignard reaction was carried out at 60°, no solid product was obtained, even after an attempted chromatographic separation of the reaction mixture.

Treatment of 10,10-Diphenyl-9,10-dihydro-9-phenanthrone with Benzylmagnesium Chloride.—A solution of 3.46 g. (0.0100 mole) of 10,10-diphenyl-9,10-dihydro-9-phenanthrone (II) in 50 ml. of benzene was added to the Grignard reagent prepared from 5.7 ml. (0.050 mole) of benzyl chloride and 1.20 g. (0.050 g. atom) of magnesium in 50 ml. of ether. The pale gray-green mixture was stirred and heated for 14 hr. at 70° before being hydrolyzed with a saturated ammonium chloride solution. Following addition of chloroform to the hydrolysis mixture, the organic layer was removed, dried over sodium carbonate and concentrated. Bibenzyl was sublimed from the crude yellow solid by heating on a steam-plate. The product weighed 4.33 g., m.p. 226–236°, with previous sintering. After crystallization from benzene, the 9-benzyl-9,10-diphenyl-9,10-dihydro-9-phenanthrol (XV) melted at 236–237°, yield 4.06 g. (94%).

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.37; H, 5.97. Found: C, 90.47; H, 6.29.

The infrared spectrum exhibits absorption assigned to a tertiary alcohol (3565, 1368, 1195 cm.$^{-1}$) and a methylene group (2955, 2935 cm.$^{-1}$). The characteristic 2840 cm.$^{-1}$ C–H absorption associated with a secondary alcohol is absent.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. I. 1,4-Pentadiene, 3-Phenylpropene and 3-Phenylcylohexene by Amine Oxide Pyrolysis[1]

BY ARTHUR C. COPE AND CARL L. BUMGARDNER[2]

RECEIVED SEPTEMBER 7, 1956

Thermal decomposition of the oxides of penten-5-yldimethylamine and 3-phenylpropyldimethylamine has been found to give 1,4-pentadiene (61%) and 3-phenylpropene (91%), respectively. Application of the Hofmann exhaustive methylation procedure to 3-phenylpropyldimethylamine yielded a mixture of olefins which vapor-phase chromatography indicated was *trans*-1-phenylpropene containing small amounts of *cis*-1-phenylpropene and 3-phenylpropene. *trans*-2-Phenylcyclohexyldimethylamine oxide on heating yielded a mixture (96%) consisting of 85% 1-phenylcyclohexene and 15% 3-phenylcyclohexene. The isomeric *cis*-amine oxide gave a mixture (72%) composed of 98% 3-phenylcyclohexene and 2% 1-phenylcyclohexene. *cis*-2-Phenylcyclohexyldimethylamine has been prepared from *cis*-2-phenylcyclohexylamine by a procedure that is more stereospecific than methylation with formic acid and formaldehyde. The primary amine was methylated with methyl iodide to form *cis*-2-phenylcyclohexyltrimethylammonium iodide, which on treatment with lithium aluminum hydride formed the tertiary amine.

Thermal decomposition of a number of alkyldimethylamine oxides previously has been shown to yield olefins by intramolecular *cis* elimination of N,N-dimethylhydroxylamine.[3,4] Although this reaction resembles the Hofmann exhaustive methylation,[5] pyrolysis of amine oxides also may be compared with ester and xanthate pyrolyses.[6] Application of the Hofmann exhaustive methylation procedure to certain amines, for example, to N-methylpiperidine[7] and to 3-phenylpropyldimethylamine[8,9] has been reported to yield conjugated olefins resulting from base-catalyzed isomerization of

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(1) Sponsored by the Office of Ordnance Research, U. S. Army, under contract no. DA-19-020-ORD-3226, Project TB2-0001 (1112). Previous research concerning amine oxides published by this group concerns the rearrangement of allyl and benzyl groups from nitrogen to oxygen in such compounds; THIS JOURNAL, **66**, 1929 (1944); **71**, 3423 (1949); and pyrolysis forming olefins and dialkylhydroxylamines, *ibid.*, **71**, 3929 (1949); **75**, 3212 (1953); **77**, 1628 (1955); **78**, 2812 (1956).

(2) United States Rubber Co. Fellow, 1954–1955.

(3) A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

(4) D. J. Cram and J. E. McCarty, *ibid.*, **76**, 5740 (1954).

(5) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

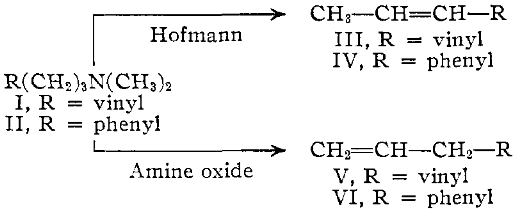
(6) E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810 (1950).

(7) A. W. Hofmann, *Ber.*, **14**, 659 (1881).

(8) L. Senfter and J. Tafel, *ibid.*, **27**, 2309 (1894).

(9) J. Weinstock, *J. Org. Chem.*, **21**, 540 (1956).

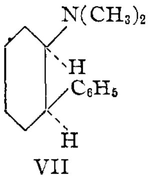
the double bond.[9,10] Ester pyrolysis, however, has been shown to proceed without subsequent rearrangement in a number of sensitive compounds.[11,12] It was of interest, therefore, to apply the amine oxide pyrolysis to cases in which the Hofmann method has been found to lead to rearranged products.



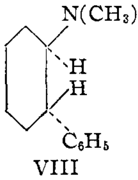
Penten-5-yldimethylamine (I) was prepared from N-methylpiperidine by application of a single Hofmann degradation.[7] As shown in the above equation, Hofmann degradation of I yields 1,3-pentadiene (III).[7] Penten-5-yldimethylamine oxide was prepared by oxidation of I with aqueous hydrogen peroxide, and the amine oxide was decomposed by heating at 57 mm. and 25–148°, forming 1,4-pentadiene (V, 61%) and N,N-dimethylhydroxylamine (isolated as the hydrochloride in 82% yield). Analysis of the ultraviolet spectrum of the diene prepared in this way indicated that a maximum of 0.2% of the conjugated isomer III was present. 3-Phenylpropyldimethylamine oxide, prepared from 3-phenylpropyldimethylamine (II) by oxidation with aqueous hydrogen peroxide, decomposed on heating at 9 mm. and 36–160° and yielded 3-phenylpropene (VI, 91%) which had an ultraviolet spectrum essentially identical with the spectrum previously reported.[13] A vapor-phase chromatogram of VI prepared in this way showed that it did not contain *cis*- or *trans*-1-phenylpropene. Decomposition of 3-phenylpropyltrimethylammonium hydroxide at 0.4–0.9 mm. and 75–120° gave a mixture of olefins (96%) which was chromatographed in the vapor phase on a silicone–Celite column at 160°. Analysis of the chromatogram indicated that the mixture consisted of 94% of *trans*-1-phenylpropene, 5% of *cis*-1-phenylpropene and 1% of 3-phenylpropene.[14] Reduction of the contact time between the olefin product and unchanged quaternary base by dropwise decomposition of 3-phenylpropyltrimethylammonium hydroxide according to a procedure described by Weinstock[9] yielded a mixture which vapor-phase chromatography showed to contain 81% *trans*-1-phenylpropene, 8% *cis*-1-phenylpropene and 11% 3-phenylpropene. This increase in the proportion of the unconjugated isomer is in qualitative agreement with the findings of Weinstock.[9]

From these results it appears that the thermal decomposition of amine oxides to olefins in contrast to the Hofmann exhaustive methylation route may be used without migration of a double bond in the type of structures discussed above.

A study of the thermal decomposition of the amine oxides obtained from *cis*- and *trans*-2-phenylcyclohexyldimethylamine (VII and VIII, respectively) also was undertaken. Application of the Hofmann procedure to these amines has been shown to yield only 1-phenylcyclohexene,[10] while pyrolysis of the acetates of *cis*- and *trans*-2-phenylcyclohexanol has been shown to give predominantly 3-phenylcyclohexene and 1-phenylcyclohexene, respectively (products of *cis* elimination).[6] *trans*-2-Phenylcyclohexylamine was prepared according to the procedure of Nightingale and Tweedie[15] and methylated with formic acid and formaldehyde in a manner previously described.[10] Oxidation of the tertiary amine VIII with aqueous hydrogen peroxide in methanol gave the amine oxide, which decomposed on heating at 10–3 mm. and 70–140°, yielding a mixture of 1- and 3-phenylcyclohexene (96%). The mixture, according to an analysis of the ultraviolet spectra, was composed of 85% of 1-phenylcyclohexene and 15% of 3-phenylcyclohexene, a composition very similar to that obtained by pyrolysis of *trans*-2-phenylcyclohexyl acetate and xanthate.[6] Of the two *cis*-β-hydrogen atoms available in the oxide of VIII, it is evident that the benzyl hydrogen atom is removed preferentially.



VII



VIII

Preparation of *cis*-2-phenylcyclohexylamine was carried out according to the directions of Arnold and Richardson.[10] Methylation with formic acid and formaldehyde by their procedure gave VII. The infrared spectrum of VII prepared in this way had a band in the carbonyl region (at 5.95μ) and the after-run from distillation of the tertiary amine gave a positive ketone test with 2,4-dinitrophenylhydrazine reagent. A ketone might arise in such a reaction from a tautomeric shift involving intermediates of the type $R_2CH-\underset{|}{\overset{\oplus}{N}}=CH_2$ and $R_2C=\underset{|}{\overset{\oplus}{N}}-CH_3$, followed by partial hydrolysis of the latter structure.[16] If such shifts occur, some inversion of the amino group to the more stable *trans* form might also be expected during the preparation of VII. Attempts to establish the purity of VII (freedom from the *trans* isomer) were inconclusive. Although there were strong bands in the infrared

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[10] R. T. Arnold and P. N. Richardson, THIS JOURNAL, **76**, 3649 (1954).

[11] L. E. Schniepp and H. H. Geller, *ibid.*, **67**, 54 (1945).

[12] W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **77**, 1163 (1955).

[13] T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, *ibid.*, **69**, 880 (1947).

[14] Weinstock (ref. 9) has reported that Hofmann exhaustive methylation of II at 10–20 mm. and 120–130° gave a mixture composed of 91% of 1-phenylpropene (presumably *trans*) and 9% of 3-phenylpropene. The composition was calculated by interpolating the index of refraction of the olefin mixture between the values of 3-phenylpropene and propenylbenzene (presumably *trans*). The value used for propenylbenzene, n^{25}_D 1.5491, is somewhat higher than that reported in ref. 23 for *trans*-1-phenylpropene (n^{25}_D 1.5473) or *cis*-1-phenylpropene (n^{25}_D 1.5400). This analysis of the mixture by refractive index is inaccurate because it does not take into account the presence of *cis*-1-phenylpropene.

[15] D. Nightingale and V. Tweedie, THIS JOURNAL, **66**, 1968 (1944).

[16] H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

spectrum of VII which were absent in the spectrum of VIII, no strong bands could be found in the spectrum of VIII which were missing in the spectrum of VII. The methiodides, prepared from VII and VIII according to the procedure of ref. 10, did not show a melting point depression on admixture. A less ambiguous synthesis of VII was consequently undertaken beginning with *cis*-2-phenylcyclohexylamine, which had been prepared by a stereospecific synthesis (the Curtius reaction) from crystalline *cis*-2-phenylcyclohexanecarboxylic acid.[10] The primary amine was exhaustively methylated with methyl iodide to give *cis*-2-phenylcyclohexyltrimethylammonium iodide, which was purified by recrystallization. Removal of methyl iodide from the methiodide by refluxing it with lithium aluminum hydride in tetrahydrofuran gave VII in 78% yield.[17] The infrared spectrum of VII prepared by this method contained no band at 5.95μ and showed very weak bands at 17.85 and 18.75μ and a shoulder at 13.3μ, which were significantly less intense than those bands occurring at the corresponding places in the spectrum of VII prepared by methylation with formic acid and formaldehyde. Since the infrared spectrum of VIII has strong bands at the above wave lengths, it appears that the amine prepared by way of its methiodide contains less of the *trans* isomer. Decomposition of the amine oxides derived from the tertiary amine prepared by the two routes corroborates this conclusion. The oxide of VII, obtained by oxidation of the amine prepared by methylation with formic acid and formaldehyde, decomposed on heating at 3–0.1 mm. and 90–175° and gave a mixture of 1- and 3-phenylcyclohexene (76%) which consisted of 91% of 3-phenylcyclohexene and 9% of 1-phenylcyclohexene according to analysis of the ultraviolet spectra. Decomposition of the amine oxide derived from the amine prepared from its methiodide gave a mixture (72%) consisting of 98% of 3-phenylcyclohexene and 2% of 1-phenylcyclohexene. 3-Phenylcyclohexene would be expected to be the sole olefin resulting from decomposition of pure *cis*-2-phenylcyclohexyldimethylamine oxide if only the *cis*-β-hydrogen atom were removed in the elimination of N,N-dimethylhydroxylamine. The presence of 1-phenylcyclohexene in the mixture may, therefore, be due to some *trans* elimination or to decomposition of any *trans*-amine oxide present as an impurity. Since pure 3-phenylpropene could be prepared by pyrolysis of 3-phenylpropyldimethylamine oxide, it seems unlikely that the 1-phenylcyclohexene was formed by partial isomerization of 3-phenylcyclohexene. These results may be compared with the previously reported pyrolysis of *cis*-2-phenylcyclohexyl acetate, which gave a mixture composed of 92.8% of 3-phenylcyclohexene and 7.2% of 1-phenylcyclohexene; the xanthate gave 96–100% of 3-phenylcyclohexene.[6] The thermal decomposition of the oxides of VII and VIII, therefore, affords further evidence that amine oxide pyrolysis involves *cis* elimination of dialkylhydroxylamine, a fact best explained on the basis of an intramolecular cyclic process.

Experimental[18]

1,4-Pentadiene (V).—To 2.72 g. of penten-5-yldimethylamine[7] was added slowly (15 min.) with cooling 5.44 g. of 30% hydrogen peroxide solution. After stirring for 18.5 hr. the mixture had become homogeneous, and an aqueous suspension of approximately 0.05 g. of platinum black[19] was added with cooling to decompose the excess hydrogen peroxide. After stirring for 5 hr., evolution of oxygen was no longer observed, and the mixture was filtered and the filtrate concentrated to a clear, colorless, viscous sirup at 10–15 mm. with a bath temperature of 40–50°. The residue was heated in a nitrogen atmosphere at 57 mm. in a round-bottomed flask connected through a short Vigreux column to two traps in series, the first cooled with Dry Ice–acetone and the second with liquid nitrogen. The flask was heated from 25 to 148° over a period of 85 min., at which time practically no residue remained. The distillate was shaken with 30 ml. of cold heptane and the heptane solution, after drying over magnesium sulfate, was distilled through a semimicro column. The first fraction was collected in a receiver cooled in Dry Ice–acetone and consisted of 1.0 g. (61%) of 1,4-pentadiene, b.p. 23–25°, $n^{20}\text{D}$ 1.3876, $\lambda_{\max}$ 224.5 mμ ϵ 51 (isoöctane). The infrared spectrum of a gaseous sample at 50 mm. was the same as that of an authentic sample.[20] The tetrabromide melted at 85.2–86.4°.[11] Assuming that the absorption at 224.5 mμ was due solely to 1,3-pentadiene ($\lambda_{\max}$ 223.5 mμ, ϵ 25,500 in hexane),[21] the ultraviolet spectrum indicated that 0.2% of 1,3-pentadiene was present. From a similar experiment, N,N-dimethylhydroxylamine hydrochloride, m.p. 100.3–105.6° (sealed capillary), was isolated in 82% yield by the following procedure. After removal of the heptane solution the aqueous solution was acidified by addition of hydrochloric acid and concentrated under reduced pressure. The residual N,N-dimethylhydroxylamine hydrochloride was dried by adding ethanol and removing it under reduced pressure.

3-Phenylpropene (VI).—A solution of 3-phenylpropanol in pyridine was treated with *p*-toluenesulfonyl chloride at 7–12° to form 3-phenylpropyl tosylate. A benzene solution of the crude tosylate was allowed to react with an excess of dimethylamine at room temperature giving 3-phenylpropyldimethylamine (86% over-all), b.p. 95–96° (10 mm.), $n^{25}\text{D}$ 1.4961.[8] To 10.0 g. of 3-phenylpropyldimethylamine was added slowly (25 min.) with cooling 14 g. of 30% hydrogen peroxide solution. After stirring at room temperature for 22 hr. the mixture had become homogeneous. The excess hydrogen peroxide was decomposed by stirring the solution with platinum black for 36 hr., at which time no further evolution of oxygen was observed. The platinum black was separated and the filtrate was concentrated to a viscous sirup at 10–15 mm. with a bath temperature of 40–45°. The sirup was concentrated to a glassy solid by drying at 0.45 mm. for 66 hr. The 3-phenylpropyldimethylamine oxide was heated in a nitrogen atmosphere at 9 mm. in a manner similar to the one described above for the decomposition of penten-5-yldimethylamine oxide. The reaction flask was heated from 36 to 160° over a period of 2 hr., the decomposition of the amine oxide beginning at about 95°. Sufficient water was then added to the distillate to bring the organic phase into the neck of the receiver, and the layer of oil was removed with a capillary pipet. After drying by cooling with Dry Ice–acetone and decanting from the ice which formed, the colorless oil was distilled through a semimicro column, yielding 6.24 g. of 3-phenylpropene, b.p. 72.5–73.5° (45 mm.), $n^{25}\text{D}$ 1.5071–1.5075, $\lambda_{\max}$ 249 mμ

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[17] Based on a procedure to be published by A. C. Cope and M. A. P. Meisinger.

[18] Melting points are corrected and boiling points are uncorrected. Infrared spectra from 2 to 16μ were determined with either a Baird double beam recording spectrometer, model B, or a Perkin-Elmer Model 21 spectrometer with a sodium chloride prism. Infrared spectra from 12 to 26μ were determined with a Baird double beam recording spectrometer with a potassium bromide prism. Ultraviolet spectra were determined with a Cary ultraviolet recording spectrophotometer, model 11 MS. We are indebted to Dr. W. R. Moore and Mr. N. A. LeBel for their assistance and advice in performing the vapor-phase chromatography.

[19] R. Feulgen, *Ber.*, **54**, 360 (1921).

[20] Am. Pet. Inst. Spectrogram No. 450.

[21] H. Booker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

(ϵ 128, in 95% ethanol), 253.8 (180), 255 (179), 259 (214), 261.5 (221), 264.3 (169), 268.2 (179)[13,22] and 0.16 g. (1.6%) of 3-phenylpropyldimethylamine. An additional 0.35 g. of 3-phenylpropene was extracted with ether from the aqueous phase which remained after removal of the organic layer. The total yield of 3-phenylpropene was 6.59 g. (91%).

Vapor-phase chromatography (described below) indicated that the 3-phenylpropene prepared by this method was free of *cis*- and *trans*-1-phenylpropene.

Decomposition of 3-Phenylpropyltrimethylammonium Hydroxide. (a).—3-Phenylpropyltrimethylammonium iodide, m.p. 178.5–180°,[8] was prepared in essentially quantitative yield by adding an excess of methyl iodide to II in anhydrous ether. A solution of 9.10 g. of the methiodide in 100 ml. of water and 25 ml. of methanol was passed through a column containing 150 ml. of the ion exchange resin IRA-400 (hydroxide form) and the quaternary hydroxide was eluted with 200 ml. of 1:1 water–methanol followed by 200 ml. of water. The eluate was concentrated under reduced pressure at 40–60° to a volume of 12 ml. The resulting viscous oil was heated during 1 hr. from 75–120° in a nitrogen atmosphere at 0.4–0.9 mm. in the apparatus described above for the decomposition of penten-5-yldimethylamine oxide. To the distillate was added 75 ml. of ether and the ether extract was washed with 50 ml. of water, 50 ml. of cold 10% hydrochloric acid solution, 50 ml. of 5% sodium bicarbonate solution and 50 ml. of water. The ether solution was dried over magnesium sulfate and distilled through a semimicro column yielding 3.38 g. (96%) of phenylpropenes, b.p. 90–92° (45 mm.), $n^{25}\text{D}$ 1.5401–1.5470. The infrared spectra of the more volatile fractions showed bands at 10.1 and 6.15 μ (characteristic of 3-phenylpropene) and a band at 13.05 μ (characteristic of *cis*-1-phenylpropene) in addition to those bands present in the spectrum of *trans*-1-phenylpropene.[23] The composition according to graphical integration of the vapor-phase chromatogram obtained as described below was 94% *trans*-1-phenylpropene, 5% *cis*-1-phenylpropene and 1% 3-phenylpropene.

(b).—A solution of 15.25 g. of 3-phenylpropyltrimethylammonium iodide in 50 ml. of methanol and 170 ml. of water was stirred with 12 g. of silver oxide for 11 hr. The solid material was separated by filtration and washed with water. The filtrate was concentrated under reduced pressure to a volume of 120 ml. and the 3-phenylpropyltrimethylammonium hydroxide was decomposed dropwise according to the procedure of Weinstock.[9] Vapor-phase chromatography (described below) indicated that the olefin product consisted of 81% of *trans*-1-phenylpropene, 8% of *cis*-1-phenylpropene and 11% of 3-phenylpropene. The infrared spectra were similar to those described above in (a).

Vapor-phase Chromatography of Mixtures of *cis*- and *trans*-1-Phenylpropene and 3-Phenylpropene.—Approximately 0.01-ml. samples were injected into a 184 × 0.6-cm. column containing a mixture of silicone oil (Dow Corning 550) and 100–200 mesh Celite in a ratio of 3:7. The column was heated to 160° and equipped with a preheater held at 115–120°. Helium was used as the carrier gas. Standard samples were prepared as follows: *trans*-1-phenylpropene was obtained by Hofmann degradation of II (described above) followed by fractionation of the olefin product through a 30 × 0.5-cm. column with a band spinning at approximately 1550 r.p.m. The fraction selected had b.p. 92° (44 mm.), $n^{25}\text{D}$ 1.5475, λ_{max} 249.5 mμ, ϵ 16,700 (95% ethanol) and an infrared spectrum essentially the same as a published spectrum.[23,24] *cis*-1-Phenylpropene was prepared according to the directions given in reference 23. 3-Phenylpropene was prepared from 3-phenylpropyldimethylamine oxide as described above.

Decomposition of *trans*-2-Phenylcyclohexyldimethylamine Oxide.—The *trans*-2-phenylcyclohexyldimethylamine oxide prepared from 9.77 g. of *trans*-2-phenylcyclohexyldimethylamine[15,10] by a procedure similar to that described for oxidation of cycloöctyldimethylamine[25] was concentrated under reduced pressure and decomposed in a nitrogen atmosphere at 10–3 mm., with a bath temperature of 70–140°. The pyrolysis was carried out in the apparatus described above for the decomposition of penten-5-yldimethylamine oxide. After 1 hr. practically no residue remained and 75 ml. of water was added to the distillate. The mixture was extracted with ether, and distillation of the dried extract through a semimicro column yielded 7.33 g. (96%) of a mixture of 1- and 3-phenylcyclohexene, b.p. 97.5–101.5° (3 mm.), $n^{25}\text{D}$ 1.5578–1.5656, λ_{max} 247 mμ, ϵ 11,000 (in 95% ethanol). The infrared spectrum had weak bands at 14.9, 13.85, 12.7 and 11.4 μ (where strong bands occur in the spectrum of 3-phenylcyclohexene) in addition to those bands which are present in the spectrum of 1-phenylcyclohexene.[22] The mixture, according to the data of Mixer and Young[22] for pure 1- and 3-phenylcyclohexene, contained 85% of 1-phenylcyclohexene by analysis of the ultraviolet spectra and 88% of 1-phenylcyclohexene according to calculations based on the index of refraction.

Decomposition of *cis*-2-Phenylcyclohexyldimethylamine Oxide. (a).—*cis*-2-Phenylcyclohexyldimethylamine was prepared according to the method of Arnold and Richardson.[10] The infrared spectrum of the amine prepared in this manner contained a band at 5.95 μ and the final fraction from distillation of the amine through a semimicro column gave a positive ketone test with 2,4-dinitrophenylhydrazine reagent. The tertiary amine was oxidized to the amine oxide in a manner similar to the one described for oxidation of cycloöctyldimethylamine.[25] The *cis*-2-phenylcyclohexyldimethylamine oxide prepared from 2.29 g. of the amine was concentrated under reduced pressure and heated from 90 to 175° during 1 hr. in a nitrogen atmosphere at 3–0.1 mm. in the apparatus described above. The distillate was treated in the same manner as the distillate obtained from decomposition of the *trans*-amine oxide and yielded 1.35 g. (76%) of a mixture of 1- and 3-phenylcyclohexene, b.p. 68.5–70.5° (1.5 mm.), $n^{25}\text{D}$ 1.5433–1.5468, λ 247 mμ, ϵ 1563 (95% ethanol). Calculations based on the ultraviolet spectra indicated that the mixture contained 91% of 3-phenylcyclohexene. In addition to the bands which are present in the infrared spectrum of 3-phenylcyclohexene, the infrared spectrum of the less volatile fractions of the mixture had shoulders at 13.5, 12.5 and 10.85 μ where strong bands occur in the spectrum of 1-phenylcyclohexene.[22]

(b).—To a solution of 3.46 g. of *cis*-2-phenylcyclohexylamine[10] in 100 ml. of methanol was added 5.0 g. of sodium bicarbonate and 39 ml. of methyl iodide. The mixture was heated under reflux for 56 hr. with stirring. The cooled mixture was then concentrated to dryness under reduced pressure and the residual *cis*-2-phenylcyclohexyltrimethylammonium iodide was recrystallized twice from absolute ethanol. After drying overnight at 0.1 mm., the methiodide weighed 4.2 g. (62%) and melted at 215–216°, giving a cloudy liquid which appeared to re-solidify on further heating. *cis*-2-Phenylcyclohexyltrimethylammonium iodide prepared by the procedure of Arnold and Richardson[10] showed the same melting point behavior, which was unchanged by addition of *trans*-2-phenylcyclohexyltrimethylammonium iodide, m.p. 233.6–234.6°.[10]

A mixture of 4.2 g. of *cis*-2-phenylcyclohexyltrimethylammonium iodide, prepared from the primary amine as described above, 125 ml. of dry tetrahydrofuran and 2.5 g. of lithium aluminum hydride was stirred under reflux for 72 hr. The mixture was then allowed to cool and 10 ml. of water was added dropwise with cooling. The mixture was filtered and the material on the filter was washed with 200 ml. of ether. The aqueous layer of the filtrate was separated and the ether layer was dried over magnesium sulfate. Distillation of the ether solution through a semimicro column yielded 1.92 g. (78%) of *cis*-2-phenylcyclohexyldimethylamine, b.p. 85–89° (0.7 mm.), $n^{25}\text{D}$ 1.5346–1.5354. The infrared spectrum contained no band at 5.95 μ, and showed very weak bands at 18.75 and 17.85 μ and a shoulder at 13.3 μ, all of which were less intense than the bands occurring at the corresponding places in the spectrum of the amine described above in (a). Strong bands are present at 18.75, 17.85 and 13.3 μ in the spectrum of *trans*-2-phenylcyclohexyldimethylamine prepared by the method given in references 15 and 10.

The *cis*-2-phenylcyclohexyldimethylamine prepared from its methiodide as described above was converted to the amine oxide as before. The *cis*-2-phenylcyclohexyldimethylamine oxide derived from 1.49 g. of the amine was concentrated and then heated from 97 to 170° during 40 min. in a nitrogen at-

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[22] R. Y. Mixer and W. G. Young, THIS JOURNAL, **78**, 3379 (1956).

[23] R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, *ibid.*, **75**, 4094 (1953).

[24] Am. Pet. Inst. Spectrogram No. 330.

[25] A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

mosphere at 0.85–0.2 mm. To the distillate was added 40 ml. of ether and the resulting mixture was washed with 10% hydrochloric acid solution, sodium bicarbonate solution and water. The ether solution was dried over magnesium sulfate and distilled through a semimicro column, yielding 0.83 g. (72%) of a mixture of 1- and 3-phenylcyclohexene, b.p. 78° (2.8 mm.), $n^{25}\text{D}$ 1.5432–1.5472, λ 247 mμ, ε 738 (95% ethanol). Calculations based on the ultraviolet spectra indicated that the mixture contained 98% of 3-phenylcyclohexene.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. II. Conversion to N,N-Dialkylhydroxylamines[1]

BY ARTHUR C. COPE AND HIOK-HUANG LEE

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Oxidation with peracetic acid has been shown to provide a convenient method for converting relatively unreactive tertiary amines to the amine oxides. The progress of the reaction can be followed by titration to determine loss of active oxygen from the peracetic acid. A series of seven N,N-dialkylhydroxylamines has been prepared in yields of 42–84% by pyrolysis of symmetrical tertiary amine oxides.

The thermal decomposition of N,N-dimethylalkylamine oxides is known to proceed with elimination of a β-hydrogen atom and the amine oxide group, forming an olefin and N,N-dimethylhydroxylamine.[2] In the first reported example of this type of reaction, Mamlock and Wolffenstein[3] described the decomposition of tri-*n*-propylamine oxide on heating, forming propylene and N,N-di-*n*-propylhydroxylamine. This paper reports the preparation and thermal decomposition of a number of *sym*-trialkylamine oxides, forming terminal olefins and N,N-dialkylhydroxylamines.[4]

The low-molecular weight triethylamine and tri-*n*-propylamine were readily converted to the corresponding amine oxides by treatment with 30% aqueous hydrogen peroxide. Completion of the oxidation was indicated by a negative phenolphthalein test for the amines.[2] However, oxidation of the higher homologs tri-*n*-butyl-, tri-*n*-amyl-, tri-isoamyl-, tri-*n*-hexyl- and tri-*n*-heptyl-amine by hydrogen peroxide was found to proceed slowly. Moreover, these amines failed to give a satisfactory color test with phenolphthalein or other common indicators, so that completion of the oxidation could not be determined by spot tests. It has been found possible to oxidize these less reactive tertiary amines conveniently with peracetic acid, and to follow the progress of the oxidations by iodometric titration.[5]

It has been shown previously that aliphatic amine oxides do not oxidize acidified potassium iodide to iodine.[6] It was therefore possible to oxidize tertiary amines with an excess of peracetic acid containing a known amount of active oxygen, and ascertain when the reactions were complete by removing aliquots periodically, adding potassium iodide, and titrating the liberated iodine with standard sodium thiosulfate solution. Five of the amine oxides listed in Table I were prepared by this method, which is recommended in general for the oxidation of relatively unreactive tertiary amines. The hygroscopic amine oxides were not isolated as such, but converted directly to the crystalline picrates.

The usefulness of peracetic acid as an oxidizing agent for high-molecular weight amines is illustrated by the fact that with this reagent tri-*n*-butylamine was essentially completely oxidized in four hours, while oxidation of the same amine with hydrogen peroxide required approximately seventy-two hours. The same yield of the amine oxide picrate was obtained whether or not the calculated amount of sodium acetate was added to neutralize the sulfuric acid present in commercial peracetic acid.

The results of thermal decomposition of the trialkylamine oxides are listed in Table II. The decompositions occurred at 100–150° under reduced pressure, and the N,N-dialkylhydroxylamines and olefins which formed distilled until no more of the relatively non-volatile amine oxides remained. In four cases the 1-alkenes that were formed were isolated and identified by their physical properties, including infrared spectra.

The ease of preparation of the amine oxides and of their thermal decomposition recommend this sequence as a synthetic method for *sym*-N,N-dialkylhydroxylamines. However, unsymmetrical tertiary amine oxides form mixtures of products upon thermal decomposition, since the elimination can involve the β-hydrogen atoms of any alkyl groups that are present.[7] The method of Rogers,[4] employing the thermal decomposition of N-oxides of β-dialkylaminopropionic esters and related compounds, accordingly, appears to be the method of choice for the preparation of unsymmetrical N,N-dialkylhydroxylamines.

Experimental[8]

Trialkylamine Oxides.—Triethylamine, tri-*n*-propylamine and tri-*n*-butylamine were oxidized with 30% aqueous hydrogen peroxide and the excess hydrogen peroxide was decomposed by adding platinum black by essentially the procedure described for preparing N,N-dimethylcyclooctyl-

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-3226, Project TB2-0001 (1112).

[2] A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

[3] L. Mamlock and R. Wolffenstein, *Ber.*, **33**, 159 (1900).

[4] M. A. T. Rogers, *J. Chem. Soc.*, 769 (1955), reported a similar investigation shortly after this work was completed.

[5] D. Swern in "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 392.

[6] M. Polonovski and M. Polonovski, *Bull. soc. chim. France*, [4] **39**, 1147 (1926).

[7] A. C. Cope, N. A. Le Bel, H. H. Lee and W. R. Moore, to be published.

[8] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.