N-methylanthranilic acid and potassium cyanate. This compound is reported to melt at 265°.[25]

Method B. A solution of 1.50 g. of 1-methyl-2-oxo-3-phenyl-4-imino-1,2,3,4-tetrahydroquinazoline in 250 ml. of 0.05*N* sodium methoxide in methanol was heated under reflux for 30 hr. The solution was then neutralized with dilute acetic acid, evaporated to a small volume, and cooled to give 0.77 g. (51%) of colorless crystals, m.p. 251–252°, identical in every respect with the material prepared by Method A above.

2-Anilino-4-oxo-3,4-dihyroquinazoline (*25*). A solution of 3.50 g. of 2,4-dianilinoquinazoline[19] in 500 ml. of 10% hydrochloric acid was heated under reflux for 4 hr., cooled, filtered and neutralized with sodium hydroxide. Filtration then gave 1.81 g. (68%) of colorless crystals, m.p. 258–260°. Recrystallization from ethanol raised the melting point to 261°. The product was identical with an authentic sample of 2-anilino-4-oxo-3,4-dihydroquinazoline prepared by the method of Grout and Partridge.[26]

2-Anilino 3-methyl-4-oxo-3,4-dihydroquinazoline (*23*). Method A. A mixture of 0.50 g. of 2-methylthio-3-phenyl-4-methylimino-3,4-dihydroquinazoline, 40 ml. of methanol, 20 ml. of water, and 2 ml. of 1*N* sodium hydroxide was heated under reflux for 3 hr. (in the hood). The light yellow reaction mixture was cooled and neutralized with dilute acetic acid, and then concentrated under reduced pressure to approximately 15 ml. Cooling gave 0.42 g. (94%) or colorless plates, m.p. 202–205°. Recrystallization from methanol raised the melting point to 206–207°.

Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.7; H, 5.2; N, 16.7. Found: C, 71.6; H, 5.0; N, 16.7.

Method B. To a solution of 0.50 g. of 2-anilino-4-oxo-3,4-dihydroquinazoline in 25 ml. of cold 1*N* sodium hydroxide was added 1 ml. of dimethyl sulfate, and the mixture was stirred at room temperature for 15 min. Filtration then gave 0.43 g. (81%) of crude product, m.p. 198–202°. Recrystallization from methanol raised the melting point to 206–207°. The product was identical in every respect with the product obtained by Method A above.

3-Methyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline (*24*). A solution of 1.00 g. of 2-anilino-3-methyl-4-oxo-3,4-dihydroquinazoline in 150 ml. of 1*N* sodium hydroxide was heated under reflux for 8 hr. with stirring. The clear, pale yellow solution was cooled, neutralized wih acetic acid, and chilled overnight. Filtration then gave 0.47 g. (68%) of a colorless solid, m.p. 241–243°. The melting point was raised to 244–245° by recrystallization from methanol. This compound was previously reported to melt at 230–233°.[27] Comparison of the reaction product with an authentic sample of 3-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline showed them to be identical.

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[25] S. Mayeda, *J. Pharm. Soc. Japan*, No. 417, 17 (1916).

[26] R. J. Grout and M. W. Partridge, *J. Chem. Soc.*, 3540 (1960).

[27] M. T. Bogart and G. Scatchard, *J. Am. Chem. Soc.*, 41, 2052 (1919).

Formation of 1-Methylcyclopentene in the Thermal Decomposition of *N*,*N*,*N*-Trimethylcyclopentylmethylammonium Hydroxide[1]

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It has been shown that the 1-methylcyclopentene formed as a by-product in the thermal decomposition of *N*,*N*,*N*-trimethylcyclopentylmethylammonium hydroxide is produced from the initial product formed by β-elimination, methylenecyclopentane, by base-catalyzed isomerization. This conclusion was reached by study of the decomposition of deuterium-labeled quaternary bases and by decomposition of *N*,*N*-dimethylcyclopentylmethylamine oxide in the presence of potassium hydroxide.

The thermal decomposition of *N*,*N*,*N*-trimethylcyclopentylmethylammonium hydroxide produces varying amounts of 1-methylcyclopentene in addition to the expected methylenecyclopentane.[4] It appeared that the formation of the abnormal olefin could be explained by the operation of one or more of three mechanisms. Two of these would involve direct formation of the compound by bimolecular eliminations accompanied by hydride shifts, while the third is the seemingly obvious possibility that the initially formed methylenecyclopentane isomerizes during the pyrolysis in the strongly basic reaction medium.

Methylenecyclopentane, however, failed to isomerize when heated at 150° for forty-eight hours in a sealed tube in the presence of 40% aqueous tetramethylammonium hydroxide. Attempts to minimize the contact of methylenecyclopentane with base and thereby decrease the amount of 1-methylcyclopentene produced the opposite result. Thus, when a concentrated solution of the quaternary base was added dropwise to a heated evacuated flask, it was found that the olefins were formed in good yield and that the ratio of the *endo* to the *exo* isomer was much higher than that found when the pyrolysis was carried out in the usual manner. In addition, it was shown that, when the pyrolysis was carried out at 0.05 and 0.01 mm. pressure rather than at 12 mm. (the pressure usually employed), the highest yields of olefins as well as the highest proportion of the abnormal product were obtained (see Table I).

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[2] National Institutes of Health Fellow, 1960–1961.

[3] Postdoctoral Fellow, 1957.

[4] A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *J. Am. Chem. Soc.*, 79, 4729 (1957).

These results raised the suspicion that 1-methylcyclopentene had indeed formed directly either through a β-elimination accompanied by a 1,3-hydride shift or by a γ-elimination accompanied by a 1,2-hydride shift.[4]

To test the former possibility cyclopentane-1,1-dicarboxylic acid-d_2 was pyrolyzed, forming cyclopentane-1-*d*-1-carboxylic acid, which was converted to *N*,*N*-dimethylcyclopentane-1-*d*-carboxamide by treatment with thionyl chloride followed by dimethylamine. The carboxamide was reduced with lithium aluminum hydride to *N*,*N*-dimethylcyclopentylmethylamine-1-*d*. Direct quaternization of this compound with methyl iodide afforded the methiodide containing 1.06 atoms of deuterium per molecule.[5] Treatment with silver oxide in water afforded the quaternary base, which was pyrolyzed. It was found that the methylenecyclopentane and 1-methylcyclopentene formed contained 0.03 and 0.06 atom of deuterium per molecule, respectively.[5] *N*,*N*-Dimethylcyclopentylmethylamine, isolated from the product mixture in 57% yield (46% after distillation), contained 1.09 atoms of deuterium per molecule.[6] These facts show that the reaction proceeds *via* a β-elimination mechanism.

In order to test the involvement of a 1,3-hydride shift during the β-elimination process, cyclopentanone was repeatedly equilibrated with deuterium oxide in the presence of potassium carbonate[7] and the cyclopentanone-2,2,5,5-d_4 was reduced to the corresponding cyclopentanol with lithium aluminum hydride at −72°.[7] The tosylate of the alcohol was prepared[7] and converted to cyclopentane-2,2,5,5-d_4-carbonitrile by treatment with sodium cyanide in dimethyl sulfoxide. The nitrile was reduced to the primary amine with lithium aluminum hydride and the tertiary amine was prepared by methylation by the Clarke-Eschweiler procedure. The *N*,*N*-dimethylcyclopentylmethylamine-2,2,5,5-d_4 contained 3.94 atoms of deuterium per molecule[6] and 93% of the compound was the d_4-species.[6] The results of the deuterium analyses of the products from the pyrolysis of the methohydroxide of this amine are summarized in Table II.

These data show that 0.80 atom of deuterium per molecule is lost in the abnormal product. If the postulated mechanism had operated (β-elimination accompanied by a 1,3-hydride shift), *all* of the deuterium in the abnormal product should have been retained.

The conclusion that can be drawn from these experiments is that the reaction proceeds by β-elimination with the primary formation of methylene-cyclopentane which then undergoes isomerization forming 1-methylcyclopentene.

This assumption was proved by an experiment in which the *N*-oxide of *N*,*N*-dimethylcyclopentylmethylamine was pyrolyzed in the presence of one equivalent of potassium hydroxide. It has been shown previously[4] that this amine oxide affords methylenecyclopentane as the only olefinic product and it was also proved[8] that the presence of a strong base does not affect the direction of elimination in *N*-oxide pyrolysis. In the present experiment, the product mixture contained 14% of 1-methylcyclopentene which must have arisen from isomerization of methylenecyclopentane.

This result contradicts the earlier finding that the *exo* olefin fails to undergo change in the presence of base; this contradiction, however, is superficial. In the Hofmann elimination the reaction proceeds from a homogeneous mixture of water and the quaternary base to a heterogeneous mixture of olefins, tertiary amine, water, and unchanged quaternary base. It seems very likely that earlier attempts to isomerize methylenecyclopentane failed because reaction conditions approaching those actually obtaining during the Hofmann elimination were not established. On the other hand, the intimate mixture of base and the *N*-oxide does approximate the actual conditions of the Hofmann elimination reaction and therefore the isomerization of newly formed or forming methylenecyclopentane by base occurs.

Experimental[9]

N,N-Dimethylcyclopentylmethylamine was obtained by the method of Cope, Bumgardner, and Schweizer,[4] b.p. 150°, $n^{25}\mathrm{D}$ 1.4389 (lit.,[4] b.p. 149.5°, $n^{25}\mathrm{D}$ 1.4385).

N,N-Dimethylcyclopentylmethylamine-1-d. Diethyl cyclopentane 1,1-dicarboxylate was converted to cyclopentane-1-*d*-1-carboxylic acid (40% over-all yield) by the sequence of conversions involving the dicarboxylic acid, the diacid chloride, and the dideutero dicarboxylic acid.[10] The crude α-deutero acid was shaken with water and taken up in ether. The ether solution was dried and concentrated, and the residue was distilled, giving cyclopentane-1-*d*-1-carboxylic acid, b.p. 85–86° (3.3 mm.), $n^{25}\mathrm{D}$ 1.4508 (lit.,[4] b.p. 121.5–122.0° at 20 mm., $n^{25}\mathrm{D}$ 1.4512). The acid chloride (b.p. 78° at 40 mm., $n^{25}\mathrm{D}$ 1.4600), obtained by treatment of the acid with thionyl chloride, was dissolved in ether and this solution was added slowly to an ice-cold solution of dimethylamine in ether. The *N*,*N*-dimethylamide had b.p. 126–127° (24 mm.), $n^{25}\mathrm{D}$ 1.4754 (lit.,[4] b.p. 64° at 0.5 mm., $n^{25}\mathrm{D}$ 1.4759). Reduction with lithium aluminum hydride in ether furnished a 91%

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(5) Deuterium analysis carried out by the falling drop method by Mr. Josef Nemeth, Urbana, Ill.

(6) Deuterium analysis carried out by Dr. Klaus Biemann, Massachusetts Institute of Technology, by mass spectrometry using a C.E.C. Type 21-103C instrument with a heated inlet system.

(7) A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(8) A. C. Cope, N. A. Le Bel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).

(9) Melting points are corrected and boiling points are uncorrected. The infrared spectra were taken with a Perkin-Elmer recording spectrophotometer, Model 21, using a sodium chloride cell. Gas chromatographic analyses were carried out using 190 × 0.8-cm. Pyrex columns containing 30% by weight of the stationary phase (as specified) on 48–100 mesh Johns-Manville Chromosorb. The samples were eluted from the columns by helium gas at 15 p.s.i. and detected with a thermal conductivity cell.

(10) C. C. Price, E. L. Eliel, and R. J. Convery, *J. Org. Chem.*, **22**, 347 (1957).

TABLE I

Results of the Pyrolyses of *N,N,N*-Trimethylcyclopentylmethylammonium Hydroxide under Different Conditions[a]

Reaction	Pressure, Mm.	Bath Temp.	Olefin Composition exo, %	endo, %	Olefin Yield, %	Amine Yield, %
1	12	160	94	6	50	29
2	0.05–0.01	70–135	64	36	58	18
3[b]	0.5–0.05	160	71	29	45	30
4[c,d]	40	100–160	83	17	27	57
5[d,e]	0.03	90–145	76	24	44	—[f]

[a] Yields are based on the methiodides and are average values obtained in two pyrolyses unless otherwise indicated. [b] The quaternary hydroxide was added dropwise to the evacuated and heated pyrolysis vessel. [c] The reaction was carried out with the methiodide derived from *N,N*-dimethylcyclopentylmethylamine-1-*d*. [d] Results from a single pyrolysis. [e] The reaction was carried out with the methiodide derived from *N,N*-dimethylcyclopentylmethylamine-2,2,5,5-d_4. [f] No tertiary amine was recovered.

TABLE II

Deuterium Analyses of the Products of the Thermal Decomposition of *N,N,N*-Trimethylcyclopentylmethylammonium Hydroxide-2,2,5,5-d_4[a]

Species, % Composition[a]	*N,N*-Dimethylcyclopentylmethylamine[b]	1-Methylcyclopentene	Methylenecyclopentane
d_1	—	0.9	—
d_2	—	6.6	1.3
d_3	6.7	70.6	10.0
d_4	93.0	21.9	87.9
d_5	0.3	—	0.8
Average D per molecule[6]	4.08	3.14	3.88
Change in D per molecule	—	−0.80	−0.06

[a] See ref. 6. [b] Used in preparation of the methiodide and methohydroxide; not a product of the thermal decomposition.

yield of *N,N*-dimethylcyclopentyl-methylamine-1-*d*, b.p. 81° (78 mm.), $n^{25}\mathrm{D}$ 1.4382. Deuterium analysis showed 0.96 atom of deuterium per molecule.[6]

N,N,N-Trimethylcyclopentylmethylammonium iodide-1-d was prepared and recrystallized from a mixture of acetone and methanol, m.p. 205.6–205.8° (no depression on admixture with an authentic sample, m.p. 205.8–206.8°[4]).

Cyclopentanone-2,2,5,5-d_4 was prepared by equilibrating cyclopentanone with nine successive portions of deuterium oxide and potassium carbonate.[7] The yield of the deuterated ketone was 44%, b.p. 128–129°, $n^{25}\mathrm{D}$ 1.4331 (lit.,[7] b.p 127°). The compound contained 3.88 atoms of deuterium per molecule,[5] and contained 91.2% of the d_4 species.[6]

Cyclopentanol-2,2,5,5-d_4 was prepared from the corresponding ketone by reduction with lithium aluminum hydride in ether solution at −72°.[7] The alcohol was obtained in 72% yield, b.p. 140°, $n^{25}\mathrm{D}$ 1.4499 (lit.,[7] b.p. 140–141°). The compound contained 3.86 atoms of deuterium per molecule,[6] and contained 85.6% of the d_4-species.[6] The tosylate, after one crystallization from pentane, melted at 28° (lit.,[7] m.p. 28–29°). It contained 3.86 atoms of deuterium per molecule.[5]

Cyclopentane-2,2,5,5-d_4-carbonitrile. A mixture of 51.8 g. of cyclopentanol-2,2,5,5-d_4 tosylate and 22 g. of dry sodium cyanide in 400 ml. of freshly distilled dimethyl sulfoxide was heated at 80° for 10 hr., after which time the mixture was cooled and poured into 1200 ml. of ice water. The resulting emulsion was extracted with three 250-ml. portions of ether, the combined ether extracts were washed with three 150-ml. portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was distilled through a semimicro column, affording 15.44 g. (73%) of the desired nitrile, b.p. 167–168°, $n^{25}\mathrm{D}$ 1.4402 (lit.,[11] b.p. of the nondeuterated compound 43–44° at 7 mm., $n^{25}\mathrm{D}$ 1.4409), containing 3.76 atoms of deuterium per molecule.[5]

N,N-Dimethylcyclopentylmethylamine-2,2,5,5-d_4 was obtained in 40% yield by reducing the nitrile with lithium aluminum hydride[12] and methylating the primary amine by the Clarke-Eschweiler procedure, b.p. 146–148°, $n^{25}\mathrm{D}$ 1.4384. The compound contained 3.94 atoms of deuterium per molecule, and 93.0% of it was the d_4-species.[6]

Thermal decomposition of the methohydroxides of N,N-dimethylcyclopentylmethylamine, N,N-dimethylcyclopentylmethylamine-1-d, and N,N-dimethylcyclopentylmethylamine-2,2,5,5-d_4. The methiodide of *N,N*-dimethylcyclopentylmethylamine-2,2,5,5-d_4. The methiodide of *N,N*-dimethylcyclopentylmethylamine was converted to the quaternary base in aqueous solution by treatment with an equivalent amount of silver oxide. The filtered solution of the base was concentrated to a thick sirup under reduced pressure at room temperature and pyrolyzed in an apparatus assembled for vacuum distillation. Two traps were used to collect the products, one cooled with a mixture of Dry Ice–acetone, the other with liquid nitrogen. The quaternary hydroxides were decomposed at the temperatures and pressures specified in Table I. The contents of the traps were dissolved in a small amount of pentane, saturated sodium chloride solution was added, and the water was removed by freezing. The pentane solution was distilled through a semimicro column. Two fractions were taken, one boiling at 65–80° and the other at 80–150°. The lower boiling fraction, containing the olefins, was analyzed by gas chromatography (21% by weight of a 67% solution of silver nitrate in tetraethylene glycol liquid phase at room temperature) to determine the composition and product ratios. Preparative gas chromatography (with the same liquid phase) was used to prepare samples for deuterium analyses wherever appropriate. The higher boiling fraction, containing trace amounts of olefins and consisting principally of the recovered tertiary amine, was analyzed by gas chromatography (Dow Corning High Vacuum Silicone Grease at 80–100°). The yields and product compositions are listed in Table I.

"Flash" decomposition of the quaternary base. A concentrated solution of the quaternary base, prepared as previously described, was added dropwise to an evacuated and heated flask assembled for distillation. The products were isolated in the manner described before. The results are listed in Table I.

Thermal decomposition of N-oxides. Solutions of the tertiary

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(11) S. M. McElvain and R. E. Starn, *J. Am. Chem. Soc.*, **77**, 4571 (1955).

(12) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

amine in methanol were oxidized by 30% aqueous hydrogen peroxide solution at room temperature. The excess peroxide was destroyed by the addition of platinum black, the mixture was filtered and concentrated to a sirup. The *N*-oxide was decomposed in the apparatus described above at 10–15 mm. pressure. The products were isolated in the manner described for the pyrolysis of the quaternary hydroxides. In two consecutive experiments methylenecyclopentane was obtained as the sole product in 43% and 56% yields, respectively. In one experiment one equivalent of potassium hydroxide in methanol was added to the *N*-oxide solution which was then concentrated and pyrolyzed in the usual manner. Methylenecyclopentane and 1-methylcyclopentene were formed in 54% and 9% yields, respectively.

Notes

4,5-Diethylphenanthrene-9,10-dicarboxylic Acid Anhydride

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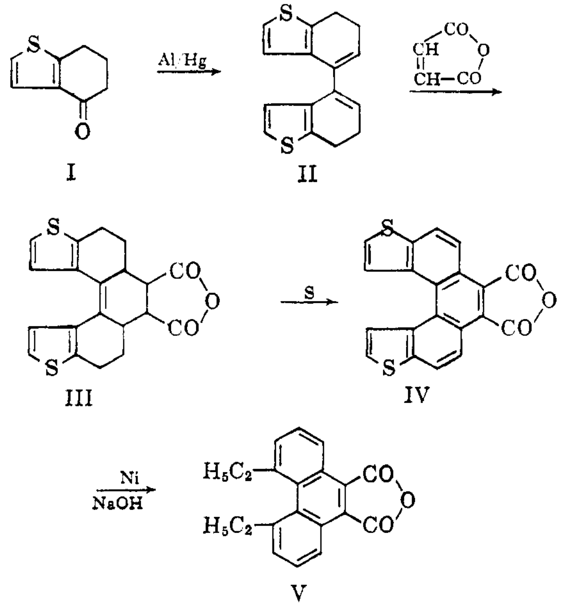
Although phenanthrene derivatives with substituents in the 4- and 5-positions have been relatively inaccessible until recently, the literature records several examples of the synthesis of 4,5-dimethylphenanthrene[1] and some of its derivatives[2] and other related molecules with substituents in hindered positions.[3]

The successful synthesis of naphthalenes and phenanthrenes containing substituent ethyl groups by desulfurization of the corresponding naphtho- and phenanthro[*b*]thiophenes[4] suggested a parallel route to phenanthrene derivatives containing ethyl groups in the 4- and 5-positions. The synthesis of 4,5-diethylphenanthrene-9,10-dicarboxylic acid anhydride has been accomplished by synthesizing a phenanthrene derivative containing two fused thiophene rings which were cleaved during the final step of the synthesis by desulfurization with Raney nickel.

Pinacolic reduction[5] of 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (I) afforded 6,7,6′,7′-tetrahydro-4,4′-bibenzo[*b*]thiophene (II) in 67% yield. Addition of maleic anhydride to the diene II in refluxing xylene solution gave a 69%-yield of the adduct, 1,2,7,8,9,10,11,12-octahydro[3,4-*b*:6,5-*b*′]dithienophenanthrene-9,10-dicarboxylic acid anhydride (III). Aromatization of III was accomplished using sulfur to yield [3,4-*b*:6,5-*b*′]dithienophenanthrene-9,10-dicarboxylic acid anhydride (IV). Desulfurization of IV in aqueous sodium hydroxide solution using Raney nickel[6] proceeded smoothly to yield 4,5-diethylphenanthrene-9,10-dicarboxylic acid anhydride (V) in 34% yield.



The assignment of the above structure to compound V is in accord with its ultraviolet spectrum which is similar to that of phenanthrene. The alternative formation of the corresponding diethyl dihydropyrene or diethylpyrene derivative is excluded on the basis of elemental analysis of compound V and the dissimilarity of its ultraviolet spectrum to those of pyrene derivatives of the type mentioned.

Experimental[7]

6,7,6′,7′-Tetrahydro-4,4′-bibenzo[*b*]thiophene (II).—To a mixture of absolute ethanol (75 ml.) and dry benzene (50

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[1] M. S. Newman and H. S. Whitehouse, *J. Am. Chem. Soc.*, **71**, 3664 (1949), G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 2326 (1950), G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953).

[2] M. S. Newman and A. S. Hussey, *J. Am. Chem. Soc.*, **69**, 3023 (1947).

[3] M. S. Newman, W. C. Sagar, and M. V. George, *ibid.*, **82**, 2376 (1960).

[4] E. J. Modest and J. Szmuszkovics, *ibid.*, **72**, 577 (1950).

[5] M. S. Newman, *J. Org. Chem.*, **26**, 582 (1961).

[6] E. Campaigne and W. E. Krieghbaum, *ibid.*, **26**, 359 (1961).

[7] Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Infrared spectra were determined as listed using a Perkin Elmer-Model 21 double beam recording spectrophotometer. Ultraviolet spectra were obtained using a Beckman DU spectrophotometer using 95% ethanol as solvent.