m.p. 74–74.5° (recrystallized from 95% alcohol). When mixed with I, obtained as described above, no depression of m.p. was observed.

1-**Phenyl-4,4-dimethyl-3,4-dihydronaphthalenol-3** (III).—To an ether solution of phenyllithium prepared from 0.92 g. (0.132 mole) of lithium pellets and 9.4 g. (0.06 mole) of bromobenzene was added 5.17 g. (0.03 mole) of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene. After refluxing for 45 minutes the reaction mixture was decomposed with iced ammonium chloride. The product was crystallized from aqueous alcohol to give a 40% yield of colorless crystals, m.p. 96–97°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.60; H, 7.08.

Dehydration-Rearrangement of III.—A 0.10-g. sample of III was allowed to stand at room temperature for 4.5 hours in 2.0 ml. of glacial acetic acid containing a drop of concd. sulfuric acid. The reaction mixture was poured into 20 ml. of cold water to precipitate 0.088 g. of a product identical with 4-phenyl-1,2-dimethylnaphthalene (I).

1,4,4-Trimethyl-1,4-dihydronaphthalenol-1 (IV).—A 10.0-g. (0.058-mole) sample of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene was added to an ether solution containing about four molar equivalents of methylmagnesium iodide. The reaction mixture was refluxed for 90 minutes and decomposed with iced ammonium chloride. The product was crystallized from petroleum ether to give 8.6 g. (78.8% yield) of colorless crystals, m.p. 83–85°.

Anal. Calcd. for $C_{13}H_{18}O$: mol. wt., 188; C, 82.93; H, 8.57. Found: mol. wt., 183; C, 82.71; H, 8.66.

This carbinol IV decolorized an ethanol solution of potassium permanganate and a carbon tetrachloride solution of bromine. On standing, the solid carbinol changed to an oil which could not be induced to crystallize. When carefully compared with IV this oil decolorized the bromine solution more rapidly. Attempted vacuum distillation of IV produced water in the Dry Ice cooled receiver, leaving a hard brittle mass in the distilling flask. No trace of 1,3,4-trimethylnaphthalene was observed.

Dehydration and Rearrangement of IV.—A 1.11-g. sample of IV was allowed to stand at room temperature for 4 hours in 15 ml. of glacial acetic acid containing one drop of concd. sulfuric acid. The reaction mixture was poured into cold water to give a semi-solid precipitate. This was taken up in ether and washed several times with dilute sodium hydroxide (nothing was base soluble). Evaporation of the ether solution gave a thick oil of which only a small portion was soluble in methanol. The methanol extract was treated with a methanol solution of picric acid to give a small amount of bright, orange, long needles, m.p. 145–148°; mixed with an authentic sample of the picrate of 1,3,4-trimethylnaphthalene, m.p. 146–148°.[9] The majority (98%) of the product from the dehydration was a thick, alcohol insoluble oil which was not investigated further.

Absorption Spectra.—Measurements were made with heptane solutions using a Beckman model D.U. quartz spectrophotometer over the range of 220–400 mμ. See Fig. 1 for the curves.

Summary

1. A new rearrangement of a retropinicol type and related to the dienol–semibenzene–benzene changes investigated by v. Auwers[5] has been studied with 1-methyl- and 1-phenyl-4,4-dimethyl-1,4-dihydronaphthalenol-1. In the latter case a good yield of the 1,3,4-trisubstituted naphthalene resulted, while in the former the major course of the reaction was a polymerization. These changes are acid catalyzed.

LINCOLN, NEBRASKA RECEIVED JULY 20, 1950

[CONTRIBUTION FROM THE AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Endocyclic α,β-Unsaturated Ketones. II.[1] Reactions of 8-Bromoperinaphthenone-7 with Amines

BY NORMAN H. CROMWELL, DAVID B. CAPPS AND S. EDWARD PALMER

It was the main objective of the present work to investigate the reactions of an endocyclic α-bromo-α,β-unsaturated carbonyl system with amines to discover whether or not the stereochemical restrictions imposed by such an arrangement greatly affect the course of such reactions. 8-Bromoperinaphthenone-7 has been found to react with the amines, morpholine and piperidine to produce both 8-amino- and 9-aminoperinaphthenone-7 derivatives. The 8-amino products were also obtained from 8,9-epoxyperinaphthanone-7. A comparison of their ultraviolet-visible absorption spectra, and their acid hydrolysis products serve to distinguish and identify the members of these two new classes of α-amino and β-amino-α,β-unsaturated ketones. The infrared spectra of the two series of compounds are reported from 1100–3400 cm.$^{-1}$ and found to be somewhat similar. With a primary amine, cyclohexylamine, 8-bromoperinaphthenone-7 gives a single racemic ethylene imine ketone. Stereoisomerism at nitrogen was not observed. The ethylene imine ketone readily reacts with acid to produce the isomeric 8-aminoperinaphthenone-7. It may be concluded that it is not a necessary requirement that the initial addition to the 1,4-unsaturated system involve a proton transfer from nitrogen to oxygen *via* a quasi six-membered ring. The results indicate however, that the opportunity for such a proton transfer, which is available in the open chain series, is a facilitating factor.

Extensive studies of the reactions of open chain α-bromo-α,β-unsaturated ketones with amines have been reported.[2] No careful study of the reactions of amines with an endocyclic system of this type has been reported previously in the chemical literature.[3] One of the most readily available starting materials for such studies is 8-bromoperinaphthenone-7. This compound is the nearest possible cyclic analog to α-bromobenzalacetophenone, with which many of the previous studies have been made. In contrast to this latter substance[2] 8-bromoperinaphthenone fails to react even at room temperature with one or two molar equivalents of morpholine, piperidine or cyclohexylamine in ether or ethanol solution. In all cases a large excess of the amine was required for the reaction to take place even in the absence of solvent. In the present studies it was not possible to isolate the probable intermediate α-bromo-β-aminoketone,[2] 8-bromo-9-aminoperinaphthanone-7, (A).

At room temperature 8-bromoperinaphthenone-7 reacted with an excess of morpholine and piperidine to give mainly the 9-morpholino and 9-piperidinoperinaphthenone-7, III and IV, respectively.

(1) For the first paper in this series see Cromwell, Eby and Capps, THIS JOURNAL, **72**, 1224 (1950).

(2) See for example, Cromwell, *Chem. Revs.*, **38**, 83 (1946).

(3) In a U. S. Patent No. 2,174,751, Oct. 1939, *Chem. Abstracts*, **34**, 1194 (1940), assigned to General Aniline Works, Inc., New York, Koeberle, Rohland and Steigerwald reported the preparation of 8-aminoperinaphthenone-7 compounds from 8-halo-perinaphthenone-7. The conditions used were different from those employed in the present work and the purity and identity of the products were not rigorously established in the publications.

Smaller amounts of 8-morpholino and 8-piperidinoperinaphthenone-7, I and II, respectively, also resulted from these reactions. At elevated temperatures the 8-aminoperinaphthenone-7 products, I and II, predominated. These latter amino ketones also resulted from the reaction of 8,9-epoxyperinaphthanone-7 with morpholine and piperidine at 80°. The structures of 8-amino- and 9-aminoperinaphthenone-7 compounds were readily differentiated. Acid hydrolysis of the former produced the known 7,8-perinaphthandione, while the latter gave the known 7,9-perinaphthandione. Moreover these two classes of unsaturated amino ketones had characteristically different visible colors and showed the expected[4] differences in their ultraviolet and visible absorption spectra, see Figs. 1 and 2.

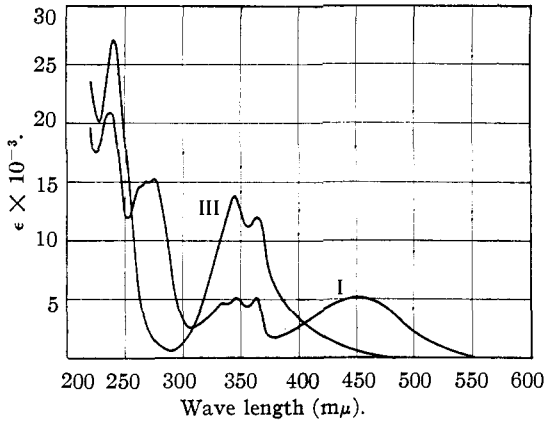


Fig. 1.—Absorption spectra of 8-morpholino (I) and 9-morpholino (III) perinaphthenone-7.

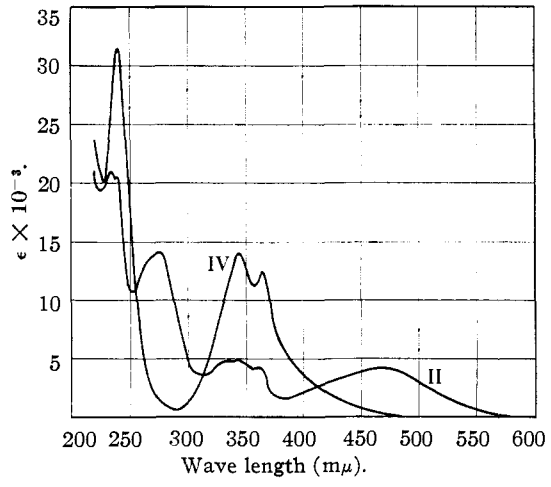
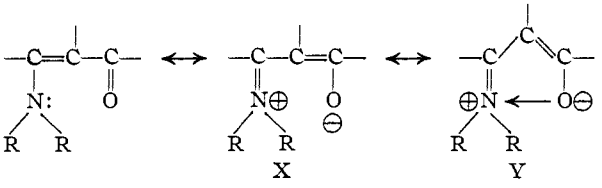


Fig. 2.—Absorption spectra of 8-piperidino (II) and 9-piperidino (IV) perinaphthenone-7.

Both the 8-amino- and 9-aminoperinaphthenone-7 compounds showed a carbonyl frequency in the infrared between 1632 and 1637 cm.$^{-1}$, see Table I. This is in sharp contrast with the findings from studies made previously with the open chain compounds.[5] For example α-morpholinobenzalacetophenone has its characteristic carbonyl band at a frequency of 1664 cm.$^{-1}$ while that of the β-morpholino isomer was located at 1628 cm.$^{-1}$. The present studies would indicate that the differences in resonance interaction of the carbonyl group electrons with those in the rest of the unsaturated system are not as pronounced in the perinaphthenone-7 system as in the benzalacetophenone series. In both the 8-amino- and 9-aminoperinaphthenone-7 compounds, considerable resonance interaction is implied by the results, but we might have expected the carbonyl band of the latter ketones to have been at a lower frequency than where it is actually found. A possible explanation is that resonance interaction within the cyclic system of type Y is impossible with endocyclic β-amino-α,β-unsaturated ketones.



It had been postulated previously[6] that structures of type (Y) might be expected to provide for maximum resonance interaction (electron mobility) in such unsaturated systems. In any case it is obvious that absorption spectra measurements in the ultraviolet and visible ranges of the spectrum are the useful ones in distinguishing the 8-amino- from the 9-aminoperinaphthenone-7 derivatives.

It was interesting to find, analogous to the behavior of α-bromobenzalacetophenone,[7] that 8-bromoperinaphthenone-7 reacted with cyclohexylamine to produce a new type of ethylene imine ketone, V, in a good yield. In contrast with 8-amino- and 9-amino-perinaphthenone-7 compounds this ethylene imine ketone was colorless. Its ultraviolet spectrum, see Fig. 3, and its carbonyl band in the infrared, see Table I, clearly indicate that it does not possess a conjugated unsaturated amino ketone system.

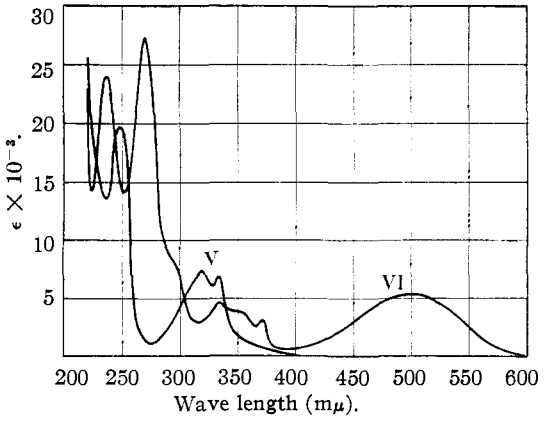


Fig. 3.—Absorption spectra of 8-cyclohexylaminoperinaphthenone-7 (VI) and 8,9-(N-cyclohexyl)-iminoperinaphthenone-7 (V).

Considerable care was taken to search for more than one isomeric form of this ethylene imine ketone

(4) Cromwell and Watson, *J. Org. Chem.*, **14**, 411 (1949).

(5) Cromwell, Miller, Johnson, Frank and Wallace, THIS JOURNAL, **71**, 3337 (1949).

(6) Cromwell and Johnson, *ibid.*, **65**, 316 (1943).

(7) Cromwell, Babson and Harris, *ibid.*, **65**, 312 (1943).

TABLE I

INFRARED ABSORPTION SPECTRA

I		II		III		IV		VI		V	
Cm.$^{-1}$	Approx. % abs.	Cm.$^{-1}$	Approx. % abs.	Cm.$^{-1}$	Approx. % abs.	Cm.$^{-1}$	Approx. % abs.	Cm.$^{-1}$	Approx. % abs.	Cm.$^{-1}$	Approx. % abs.
3045	2–3	3045	1–2	3045	2–3	3045	2–3	3045	2–3	3357	30
1637	77	3020	2–3	1633	90	2995	2–3	3030	2–3	3020	2–3
1621	79	1630	80	1611	80	1633	85	1632	78	1685	80
1585	44	1619	85	1578	93	1611	74	1615	85	1590	48
1570	65	1600	50	1554	80	1578	90	1592	79	1578	42
1508	40	1588	40	1412	32	1553	75	1512	85	1508	60
1412	15	1568	75	1356	76	1433	45	1403	33	1363	52
1327	8	1508	45	1327	31	1410	32	1348	46	1341	35
1304	13	1406	28	1300	38	1378	76	1313	30	1312	18
1268	72	1381	60	1290	30	1362	65	1302	23	1304	14
1253	25	1352	28	1259	35	1365	60	1293	35	1275	59
1230	40	1325	23	1213	73	1353	53	1268	32	1258	11
1203	50	1278	18	1203	73	1329	32	1261	28	1252	14
1182	55	1259	70	1186	35	1295	35	1253	40	1242	43
1173	35	1254	60	1170	32	1280	15	1227	35	1219	29
1154	25	1231	57	1155	33	1262	10	1199	50	1192	32
1127	54	1219	35	1147	40	1223	79	1179	31	1182	35
1119	81	1196	60	1114	83	1208	52	1164	33	1167	42
1099	43	1190	57			1164	32	1150	38	1152	38
		1154	39			1159	40	1132	30	1141	32
		1136	33			1152	36	1116	40	1109	57
		1129	33			1132	60				
		1109	45			1109	42				

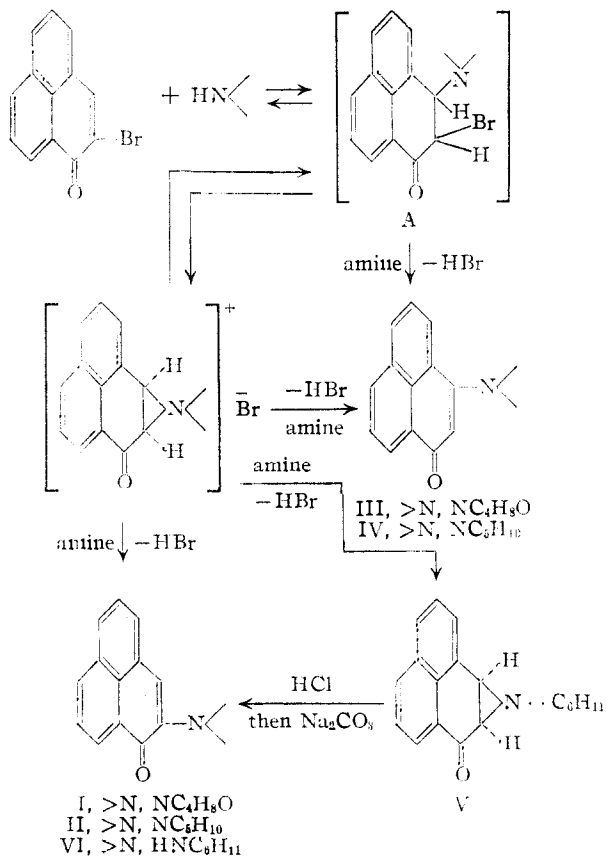
V. Neither the melting point nor the infrared spectra studies gave any evidence of more than one form. Although the perinaphthanone ring system must of necessity be fused to the three-ring in only a *cis* arrangement, it was conceivable that the cyclohexyl group might be located above or below the plane of the three-ring. However, from a consideration of the mechanism discussed below it is apparent that the three-ring would be expected to close in such a manner as to have the cyclohexyl group turn up on the side of the three-ring opposite to that of the perinaphthanone system.

The 8,9-(N-cyclohexyl)-iminoperinaphthanone-7, (V) proved to be very unstable in the presence of even acid fumes. In alcoholic hydrochloric acid the three-ring was rapidly cleaved to produce the apparently very unstable 9-chloro-8-cyclohexylaminoperinaphthanone-7, which rapidly lost hydrogen chloride to give the deeply colored 8-cyclohexylaminoperinaphthenone-7 (VI). The ultraviolet, see Fig. 3, and the infrared, see Table I, spectra of VI definitely classified it as an α-amino ketone in this series.

In contrast with the behavior of benzalacetophenone,[8] perinaphthenone-7 failed to react with morpholine.

Discussion of the Reactions.—It is interesting to observe that the products isolated from the reaction of the 8,9-epoxyperinaphthanone-7 with morpholine and piperidine were the 8-amino instead of the 9-aminoperinaphthenones.[9] Whether the 8-amino products resulted from an intermediate 8-amino-9-hydroxyperinaphthanone-7 through loss of water, or by a dehydration-rearrangement of the isomeric 8-hydroxy-9-aminoperinaphthanone-7, cannot be decided by the present experiments.

The mechanism of the reaction of open chain α-bromo-α,β-unsaturated ketones has been dis-



(8) Pollard and Stewart, THIS JOURNAL, **59**, 2702 (1937).

(9) It has previously been shown in this Laboratory that epoxybenzylacetophenone reacts with these amines at the β-position to produce the α-hydroxy-β-aminobenzylacetophenones, Cromwell and Barker, *ibid.*, **72**, 4110 (1950).

cussed previously.[2,10] The present studies with an endocyclic α-bromo-α,β-unsaturated ketone require only a slight modification of the previously proposed mechanism. It would appear that it is not a necessary requirement that the initial addition to the 1,4-unsaturated system involve a proton transfer from nitrogen to oxygen *via* a quasi six-membered ring. However, since large amounts of the amine, higher temperatures and longer reaction times are required to obtain reaction with the endocyclic system it would seem that such a proton transfer, which is possible in the open chain series, is a facilitating reaction factor.

Since both 8-amino- and 9-aminoperinaphthenone-7 compounds as well as an ethylene imine ketone were obtained in these studies it is quite evident that the initial step in these reactions involves attack by the amino group at the β-carbon atom of the 1,4-system. The formation of the β-amino-α,β-unsaturated ketones is unique and a characteristic of the behavior of this endocyclic system. The consummation of these reactions to produce the products isolated seems quite dependent upon the non-reversibility of the step involving loss of hydrogen bromide. This statement is borne out by the fact that perinaphthenone-7 failed to give an addition product with morpholine. In this latter case every step of the reaction which might be expected to produce a 9-aminoperinaphthanone-7 is reversible and the equilibrium appears to be unfavorable in this series.

Experimental[11]

Reaction of 8,9-Epoxyperinaphthanone-7 with Morpholine and Piperidine.—A 1.0-g. sample of the epoxide[12] mixed with 7 ml. of the amine was heated at 85° for 1 hour. The cooled solution was mixed with ether and extracted with several portions of 10% hydrochloric acid. The acid extract was made basic with sodium hydroxide to precipitate a red oil which was crystallized from aqueous ethanol. The reaction with morpholine gave a 50% yield of 8-morpholinoperinaphthenone-7 (I); red needles, m.p. 144–144.5°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.76; H, 5.85; N, 5.29.

The reaction with piperidine produced an 85% yield of 8-piperidinoperinaphthenone-7, II, red granules, m.p. 115–116°.

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.94; H, 6.63; N, 5.20.

Reaction of 8-Bromoperinaphthenone-7 with Morpholine and Piperidine, (1) **at 85°.**—A 1.0-g. sample of the bromide[13] was mixed with 10 ml. of the amine and the solution heated at 85° for 1 hour. To the cooled mixture was added 50 ml. of dry ether to precipitate nearly the theoretical amount of the starting amine hydrobromide. The red ethereal filtrate was extracted several times with 10% hydrochloric acid. The acid extract was made basic with sodium carbonate to precipitate a red oil which was crystallized from methanol–water mixtures. In this way the red amino ketones I and II were obtained in yields of 50 and 75%, respectively, identical with samples obtained from the epoxide reactions.

(2) **At 25°.**—A mixture of 1.0 g. of the bromide and 10 ml. of the amine was allowed to stand at room temperature in the dark for 2 days. Addition of dry ether precipitated the theoretical amount of the starting amine hydrobromide which was removed. The ethereal filtrate was washed with water and extracted with 25 ml. of 10% hydrochloric acid.

There appeared in the acid extract of the reaction mixture with morpholine an orange solid precipitate which was removed and treated with a methanol–water solution of sodium carbonate to give an oil which after recrystallization from aqueous ethanol produced a 40% yield of 9-morpholinoperinaphthenone-7 (III); yellow crystals, m.p. 139–140.5°; mixed with I, m.p. 115–138°. The residual acid extract solution on neutralization gave only a trace of I, m.p. 144–145°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found for III: C, 76.59; H, 5.46; N, 5.22.

The acid extract of the piperidine reaction mixture was made basic with sodium carbonate to give a red oily precipitate which on recrystallization from a mixture of benzene and petroleum ether produced an 80% yield of the yellow crystalline 9-piperidinoperinaphthenone-7 (IV), m.p. 122–123°.

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.34; H, 6.48; N, 5.36.

Only a trace of II, m.p. 114–116°, could be recovered from the filtrates.

Hydrolysis of 8-Morpholino and 9-Morpholinoperinaphthenone-7.—The amino ketones were dissolved in small amounts of 10% hydrochloric acid and heated to boiling for 5 minutes. In both cases a solid precipitate formed which was recrystallized from methanol. 8-Morpholinoperinaphthenone-7 gave an 80% yield of perinaphthandione-7,8; orange needles, m.p. 177–181°.[12] The 9-morpholinoperinaphthenone-7 produced a 70% yield of perinaphthandione-7,9; yellow crystals, m.p. 262° dec.[14]

8,9-(N-Cyclohexyl)-iminoperinaphthanone-7 (V).—A mixture of 1.30 g. of 8-bromoperinaphthenone-7 and 13 ml. of cyclohexylamine was allowed to stand in the dark at room temperature for 2 days. Most of the excess cyclohexylamine was removed by heating on the steam-bath under reduced pressure. The residue was mixed with dry ether and the theoretical amount of cyclohexylamine hydrobromide removed by filtration. The ether filtrate was well washed with water, dried and concentrated. The orange residue was recrystallized from methanol to give 0.97 g. of powdery, white crystals, m.p. 147–148° dec.

Anal. Calcd. $C_{19}H_{19}NO$: mol. wt., 277; C, 82.28; H, 6.91; N, 5.05. Found: mol. wt., 278; C, 81.98; H, 7.04; N, 4.97.

Several attempts to obtain reaction between 8-bromoperinaphthenone-7 and cyclohexylamine in 1:2 mole ratios in ethanol solution failed. Even when temperatures up to 100° were employed for several hours, most of the starting bromo ketone was recovered. 8-Bromoperinaphthenone-7 failed to release any iodine on 30 minutes of refluxing with acidic potassium iodide solutions.[15]

8-Cyclohexylaminoperinaphthenone-7 (VI).—A 0.66-g. sample of the ethylene imine ketone V was dissolved in a mixture of 10 ml. of ethanol and 0.44 ml. of concd. hydrochloric acid. The solution immediately turned red in color. After standing at room temperature for 12 hours about one-half of the solvent was evaporated and aqueous sodium carbonate added. The deep purple solid which precipitated immediately, was removed by filtration and recrystallized from abs. ethanol to give 0.60 g. of fine, purple needles, m.p. 116–118°.

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.02; H, 6.70; N, 5.11.

Attempted Reaction of Morpholine with Perinaphthenone-7.—One gram of the ketone was refluxed for 10 hours with 10 ml. of morpholine. After removal of the morpholine, 95% of the starting ketone was recovered.

Absorption Spectra.—The ultraviolet-visible absorption spectra were determined using heptane solutions and a Beckman model DU quartz spectrophotometer. The infrared absorption spectra were determined using Nujol mulls of the compounds and a Perkin–Elmer Infrared spectrophotometer Model 12B by Dr. H. S. Gutowsky and Miss E. M. Petersen of the University of Illinois.

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(10) Cromwell and Cram, THIS JOURNAL, **65**, 301 (1943).

(11) Microanalyses are by the Clark Microanalytical Laboratory, Urbana, Illinois, arranged for through the courtesy of the Smith, Kline and French Laboratories, Philadelphia, Pa.

(12) Fieser and Newton, THIS JOURNAL, **64**, 919 (1942).

(13) Lukin, *Bull. Acad. Sci. U. R. S. S. Classe Sci. Chem.*, 695 (1941): *C. A.*, **37**, 2735 (1943).

(14) Wojack, *Ber.*, **71B**, 1102 (1938).

(15) Cromwell and Wankel, THIS JOURNAL, **70**, 1320 (1948).