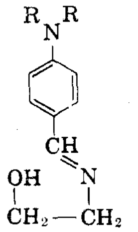

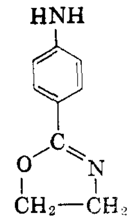

Aminophenyl-2-oxazoline

EXPERIMENTAL[12]

Materials. *p*-Dimethylaminobenzaldehyde (m.p. 72–73°) and *p*-diethylaminobenzaldehyde (m.p. 38–39°) were prepared by the method of Duff.[13] All of the following reagents were used without further purification: 2-Aminoethanol was Eastman Reagent Grade. 1-Amino-2-propanol and 2-methoxyethylamine were Eastman Practical Grade. 3-Aminopropanol, 3-methoxypropylamine, 3-isopropoxypropylamine, and 3-dimethylaminopropylamine were furnished to us by the American Cyanamid Co. 2-Amino-1-butanol was furnished by the Commercial Solvents Corp.

Preparation of the Schiff base. A mixture of 0.1 mole of the *p*-dialkylaminobenzaldehyde, 0.12 mole of the primary amino compound, and 50 ml. of dry benzene contained in a Dean-Stark moisture determination apparatus was heated under reflux in an oil bath until the volume of water collected in the trap remained constant (2–3 hr.). The benzene was removed by distillation under reduced pressure, and the residual oil was poured onto an ice water mixture. If the organic layer solidified, Process A was used; if it did not, Process B was used.

Process A. The solid crystalline mass was triturated with cold water, collected on a suction filter, and washed on the filter with several portions of cold water. After drying the crystals on the filter by use of a rubber dam followed by air drying, the crude material was dissolved in boiling petroleum ether (b.p. 30–60°), treated with Norite A for 15 min., filtered, and the filtrate was cooled in an ice-water bath to induce crystallization. The crystals were collected on a suction filter and washed with several small portions of cold petroleum ether.

Process B. The organic layer was extracted with ether, and the ethereal solution was washed several times with cold water, the washings being discarded. After drying over anhydrous magnesium sulfate and filtering, the ether was removed on a steam bath. In some instances, the residual liquid solidified after standing at room temperature for several days, and the solid product was recrystallized from boiling petroleum ether as in Process A. If the liquid did not solidify, it was purified by distillation under reduced pressure.

Infrared spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 21, using a NaCl prism. A smear was used for the liquids and a 5% solution in CCl_4 was used for the solids.

Acknowledgment. The authors wish to express their thanks to the American Cyanamid Co. and the Commercial Solvents Corp. for their generous gifts of reagents, to Dr. James J. Brader of the Noyes Laboratory for the determination and interpretation of the infrared spectra, and to Mr. Joseph G. Cannon for his many helpful suggestions and criticisms.

CHICAGO 12, ILL.

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(12) All melting points and boiling points are uncorrected.

(13) J. C. Duff, *J. Chem. Soc.*, **1945**, 276 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

Syntheses and Ultraviolet Spectra of 1-(5- and 8-Methyl-1-naphthyl)-1-cyclopentenes and 1-Cyclohexenes[1-3]

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Received July 31, 1956

Syntheses of the four 1-(5- and 8-methyl-1-naphthyl)cyclopentenes and cyclohexenes from 1-nitronaphthalene are described. The ultraviolet absorption spectral characteristics of these alkenes and of several 1,5- and 1,8-disubstituted naphthalene intermediates are presented and discussed.

In previous papers[4-6] we reported syntheses and ultraviolet absorption spectra of I, II, and their 2-naphthyl isomers as well as five derivatives (bearing methyl groups on the cycloalkenyl moiety) of these four parent naphthylcycloalkenes. The present paper extends these studies to four additional derivatives III–VI (bearing methyl groups on the naphthyl moiety).

The synthetic scheme for the 1,8-disubstituted naphthalenes III and IV is outlined herewith.

1-Nitronaphthalene was first nitrated *via* mixed acid to a mixture of 1,5- and 1,8-dinitronaphthalenes, resolved into its components by fractional crystallization. The latter isomer was reduced read-

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(1) Presented at the Northwest Regional Meeting of the AMERICAN CHEMICAL SOCIETY, Seattle, Wash., June, 1956. Paper VIII in the series on "Chemical Reactivities of Arylcycloalkenes." For preceding papers see L. H. Klemm and H. Ziffer, *J. Org. Chem.*, 21, 274 (1956) and ref. (18).

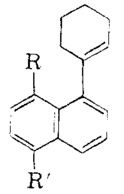
(2) Performed under the sponsorship of the Office of Ordnance Research, U.S. Army Contract No. **DA-04-200-ORD-176.**

(3) Abstracted largely from the M.A. and Ph.D. dissertations of J. W. Sprague, University of Oregon, 1954 and 1955, respectively.

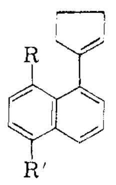
(4) L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

(5) L. H. Klemm and H. Ziffer, *J. Org. Chem.*, **20**, 182 (1955).

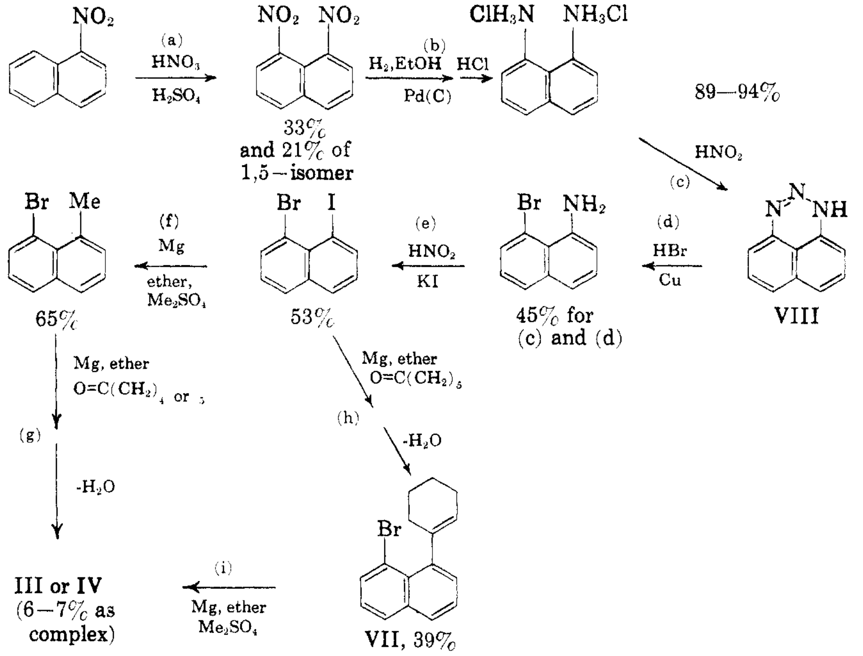
(6) L. H. Klemm, H. Ziffer, J. W. Sprague, and H. Hodes, *J. Org. Chem.*, **20**, 190 (1955).



I: R, R′ = H
III: R = CH_3; R′ = H
V: R = H; R′ = CH_3



II: R, R′ = H
IV: R = CH_3; R′ = H
VI: R = H; R′ = CH_3



ily, by means of low-pressure catalytic hydrogenation using 30% palladium-charcoal as catalyst and 95% ethanol as solvent, to 1,8-diaminonaphthalene, isolated as the crystalline dihydrochloride in excellent yield. Steps (c) to (f) followed closely the procedure of Fieser and Seligman[7] except that use of activated copper in step (d) gave inconsistent results in our hands. Meanwhile it was noted that copper turnings dissolved in refluxing 48% hydrobromic acid to give a solution which readily effected the desired transformation. Reaction of the Grignard reagent from 1-bromo-8-methylnaphthalene with cyclohexanone (or cyclopentanone), dehydration of the intermediate carbinol, and fractional distillation of the crude product gave an unusually large amount of forerun and only a very small yield of purified III or IV, isolated from the alkene fraction *via* the crystalline polynitroaromatic molecular compound. Examination of the forerun indicated that the main product formed was 1-methylnaphthalene, probably produced through preferential abstraction of hydrogen from the cycloalkanone by the sterically hindered Grignard reagent. Consistent with this interpretation are the findings of Fieser and Seligman[7] that this same Grignard reagent produced better yields of addition products with *o*-chlorobenzaldehyde (44%) and phthalic anhydride (66%), where no α-hydrogens are present, than with the enolizable *o*-chloroacetophenone (20% after dehydration). In an effort to circumvent reduction of this Grignard reagent we investigated the alternate route involving steps (h) and (i). Though a fair yield of crystalline 1-(8-bromo-1-naphthyl)cyclohexene (VII) (plus 16% of 1-bromonaphthalene) was obtainable in the former step, the subsequent methylation proceeded poorly. A pure intermediate was not obtained when cyclopentanone was used in step (h).

Much better success was attained in syntheses of the sterically less hindered 1,5-disubstituted naphthalenes V and VI, *via* the scheme.[8]

The product from bromination of molten 1-nitronaphthalene was reduced with iron (theoretical quantity) and acidulated water to 5-bromo-1-naphthylamine, transformed first to 1-bromo-5-iodonaphthalene (72% yield, by diazotization in a mixture of glacial acetic and concentrated sulfuric acids and rapid addition of the resultant mixture to excess aqueous potassium iodide) and then to 1-bromo-5-methylnaphthalene (35–49% yield) by the procedure used for the analogous conversion in the 1,8- series. Step (g) yielded about 40% of purified complexes of V and VI.

Pertinent data on the ultraviolet absorption maxima of III–VII and of nine intermediates prepared

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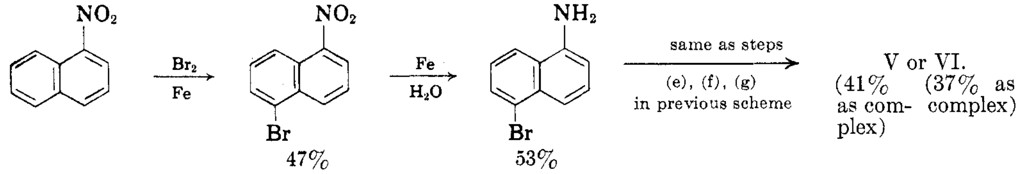
(7) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, 61, 136 (1939).

(8) Despite the availability of 1,5-dinitronaphthalene as a by-product from nitration of 1-nitronaphthalene, a synthetic scheme for V and VI exactly analogous to that used for the 1,8-isomers is precluded on the basis that a 1,5-aziminonaphthalene intermediate is sterically impossible. Such an intermediate (VIII) effectively controls stepwise diazotization and replacement of the two amino groups in the 1,8-series.



in their syntheses are given in Table I, where comparison may be made with corresponding data for 1,5- and 1,8-dimethylnaphthalenes. The absorption curves for the five compounds bearing amino or nitro groups exhibit the typical smoothness associated with conjugation[9,10] and resemble in general shape the spectra recorded for 1-nitronaphthalene [λ_{max} 243 mμ (log ε 4.02); 342 (3.59); solvent, absolute ethanol][11] and 1-naphthylamine[λ_{max} 240 mμ (log ε 4.36), 322 (3.71); solvent ethanol].[12] Variation in solvent used (especially in these cases where hydrogen-bonding may be large) interferes with a complete and meaningful comparison of results. One observes, however, that substitution of a bromine atom in the 8-position of 1-naphthylamine produces an anticipated bathochromic shift in the spectrum (7 and 20 mμ in the respective positions of the absorption maxima). Also it appears that substitution of a second nitro group into the 5- or 8- position of 1-nitronaphthalene effects a hypsochromic shift in the spectrum, *i.e.* makes the corresponding transitions more difficult—perhaps due to counteraction between the strongly electron-withdrawing nitro groups. This shift is more pronounced in the 1,8- isomer, where the nitro groups are in closer proximity than in its 1,5- counterpart.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA FOR SOME DISUBSTITUTED NAPHTHALENES[a]

Substituents in 1,5- Positions

1-C_6H_9, CH_3[b]		1-C_5H_7, CH_3[b]		CH_3, CH_3[d]		Br, CH_3[g]		Br, I[g]		Br, NH_2[b]		Br, NO_2[b]		NO_2, NO_2[g]	
λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε
										218	4.82	220	4.59	—[h]	—
229	4.86	229	4.79	227	5.13	227	4.90	230	4.78						
										245–8	4.19	245	4.35	233	4.32
(279)	3.89	(280)[c]	3.79	276	3.85	280	3.83	(288)	3.91						
287	3.99	289	3.92	286	3.95[e]	290	3.93	297	4.01						
(296)	3.90	(294–8)	3.90	298	3.80[f]	301	3.78	307	3.88						
										331	3.76	326	3.84	327	3.81

Substituents in 1,8- Positions

1-C_6H_9, CH_3[b]		1-C_5H_7, CH_3[b]		CH_3, CH_3[d]		Br, CH_3[b]		Br, I[b]		Br, NH_2[g]		Br, 1-C_6H_9[b]		NO_2, NO_2[g]	
λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} mμ	log ε	λ_{max} m_η	log ε
										—[h]	—			—[h]	—
229	4.82	229	4.81	228	5.04	230	4.84	234	4.75			228–9	4.82		
		(260)	3.39												
										247	4.34			231	4.44
(277)	3.81	(278)	3.79	275	3.80	(280)	3.71	(296)	3.93			(285–6)	3.86		
287	3.91	288	3.91	285	3.86[e]	293	3.85	306–8	4.00			293–4	3.94		
(296)	3.83	(296–8)	3.83	293	3.74[f]	(303)	3.76	(321)	3.88			(302–3)	3.88		
(321)	2.90									342	3.83			313	3.81

[a] Determined by means of a Beckman DU spectrophotometer using analytically pure samples. Parenthesized values of λ_{max} represent shoulders rather than true maxima. [b] Solvent, cyclohexane. [c] Shoulder barely discernible. [d] See reference 10, spectra 202 and 205; solvent, isoöctane. [e] Some barely perceptible shoulders in the region 250–270 mμ have been omitted. [f] Fine structure beyond this maximum has not been included in this table. [g] Solvent, ethanol. [h] From the curve it is apparent that a maximum is present at <214 mμ.

All of the other spectra investigated (Table I) have the same general shape as that of a dimethylnaphthalene (but devoid of some minor fine structure), where the substituents produce mainly a bathochromic shift in the spectrum of naphthalene in the general order of effectiveness I >> Br > cycloalkenyl ≅ Me > H.[10] It is particularly noteworthy that the spectra of III–VI are nearly identical and differ from those of their parent hydrocarbons I and II[6] essentially only in being shifted bathochromically by about 4 mμ (equal to the shift observed in going from 1-methylnaphthalene[13] to the 1,5- and 1,8-dimethylnaphthalenes). The θ′-distributions[6] (sterically unrestricted angles of twist between the planes of the naphthalene ring and the

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(9) R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

(10) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951, pp. 19–21.

(11) H. H. Hodgson and D. E. Hathway, *Trans. Faraday Soc.*, **41**, 115 (1945).

(12) Y. Hirshberg and R. N. Jones, *Can. J. Research*, **27B**, 437 (1949).

(13) Ref. (10), spectrum 196.

cycloalkenyl double bond) for I and II should not be altered by insertion of a methyl group in the 5-position of the naphthalene ring but will be decreased in extent (θ' = 80–128° for I, θ' = 90° for III) by methylation in the 8- position. The insensitivity of the spectra to such variation in θ' is consistent with our previous suggestions[6] that from the point of view of ultraviolet spectroscopy the alkenyl double bonds in I and II [as well as in III–VI] are effectively unconjugated with the naphthalene nucleus (θ- distribution = 90° ± β).

EXPERIMENTAL[14]

1-Nitronaphthalene. Technical grade 1-nitronaphthalene was recrystallized from ethanol (2 ml. per g. of nitronaphthalene), m.p. 58–60°.

Nitration of 1-nitronaphthalene. To the dark red solution of 500 g. of purified 1-nitronaphthalene in 4.1 kg. of technical grade sulfuric acid (66° Baumé) contained in a 16-l. borosilicate jar immersed in a stirred ice-salt bath was added, dropwise (over 1.5–2 hr.) with efficient stirring[15] at a reaction temperature maintained at 0–5°, 1 l. of mixed acid (prepared from 200 ml. of technical grade 36° Baumé nitric acid and 800 ml. of technical grade sulfuric acid). An additional 100–200 ml. of mixed acid was then added portionwise (over 15–30 min.) until no further red coloration was apparent on extended stirring. The mixture was poured slowly, with stirring, onto 16 l. of powdered ice and the reaction vessel was rinsed with ice-cold water. Several hours later the precipitate was collected by suction filtration, washed with 6–8 l. of hot water, and dissolved in 14 l. of hot acetone. The filtered (with a cheesecloth mat) acetone solution deposited yellow needles on cooling to room temperature. The washed (with 200 ml. of acetone) needles were recrystallized from pyridine (5 ml. per g. of crystals), yield 113–120 g. of 1,5-dinitronaphthalene, m.p. 215–216°; reported[16a] m.p. 219°.

The acetone mother liquor was concentrated to crystallization, cooled to 5°, and filtered. The collected precipitate was washed with 1 l. of ethanol, dried, and dissolved in 3 l. of hot benzene. The crystals which formed on cooling the filtered benzene solution to room temperature were recrystallized two or three times from benzene and once from glacial acetic acid (Norit A), washed with water (first cold, then hot), and dried at 110°, yield 175–190 g. of 1,8-dinitronaphthalene as pale yellow rhombs, m.p. 171–172°; reported[16b] m.p. 172°.

Processing (*via* the entire preceding crystallization scheme) of the precipitate obtained from concentrating and cooling the benzene and acetic acid mother liquors gave additional yields of 13 g. of 1,5- isomer and 25 g. of 1,8- isomer (21% and 33%, av. over-all yields, respectively).

1,8-Diaminonaphthalene dihydrochloride. A mixture of 100 g. of finely powdered 1,8-dinitronaphthalene, 2 g. of 30% palladium-charcoal, and 1 l. of ethanol, contained in a 2-l borosilicate aspirator bottle (tightly stoppered *via* a collar screw assembly and strapped horizontally into a metal can partially filled with water at 15°), was shaken mechanically in the presence of hydrogen (introduced from a reservoir *via* the side connector of the aspirator bottle) at a pressure of 1.7–4.0 atm. until the theoretical amount (6 molar quantity) of hydrogen had been absorbed. The nearly colorless solution resulting from filtration (Celite) of the reaction mixture was treated with 250 ml. of concentrated hydrochloric acid and 250 ml. of ether, chilled, and filtered. The solid was washed with ether and dried, yield 94–100 g. (89–94%) of creamy white powder, m.p. 290° (dec.); reported[16c] m.p. *ca.* 280°.

Use of Adams' platinum catalyst instead of palladium-charcoal gave a red solution and a blue-gray product. Attempts to use Raney nickel catalysts of various types and under a variety of conditions were uniformly unsuccessful.

8-Bromo-1-naphthylamine. To the solution prepared by refluxing a mixture of 60 g. (0.94 g.-atom) of copper turnings with 900 ml. of reagent grade 48% hydrobromic acid and maintained at 100–110° was added portionwise the pulverized crude aziminonaphthalene[7] obtained from a total of 198 g. (0.86 mole) of 1,8-diaminonaphthalene dihydrochloride. The mixture was then refluxed for 30 min. and processed further according to the directions of Fieser and Seligman,[7] yield 82–88 g. (43–46%), b.p. 140–150° (2 mm.), m.p. 86–88°.

1-Bromo-8-iodonaphthalene was prepared according to published directions,[7] m.p. 97–99°.

1-Bromo-8-methylnaphthalene was prepared according to Fieser and Seligman[7] except that the magnesium was added portionwise to aid in moderation of the reaction and the final product was crystallized from methanol, m.p. 74–76°, yield 65%; reported m.p. 76–78°, yield 74%.

1-(8-Bromo-1-naphthyl)cyclohexene (VII). To the Grignard reagent (prepared by initiation *via* iodine and subsequent moderation by cooling) from 33.3 g. (0.01 mole) of 1-bromo-8-iodonaphthalene, 2.4 g. (0.10 mole) of magnesium, and 100 ml. of ether was added slowly a solution of 11 ml. (0.11 mole) of cyclohexanone in 20 ml. of benzene. The mixture was stirred for 10 hr. at room temperature and then poured into excess dilute acetic acid. The nonaqueous phase, combined with ethereal extracts of the aqueous phase, was washed with water, dried, and evaporated. The residue was heated at 200° (nitrogen atmosphere) until evolution of water had ceased and then fractionally distilled to yield 12.3 g. of yellow liquid, b.p. 172–178° (2.4 mm.), which crystallized on standing. Recrystallization from methanol produced 11.1 g. (39%) of flakes, m.p. 51–53°, elevated to 55–56° on repeated crystallization of a small sample from the same solvent.

Anal. Calcd. for $C_{16}H_{15}Br$: C, 66.91; H, 5.27. Found: C, 66.28; H, 5.51.

The product decolorized bromine in carbon tetrachloride. It failed to yield a crystalline complex with either picric acid in ethanol or trinitrofluorenone in glacial acetic acid.

1-(8-Methyl-1-naphthyl)cyclohexene (III). (*a*) *From VII.* To a refluxing mixture of 30 ml. of ether, 1.4 g. (0.058 g.-atom) of magnesium, and an iodine crystal was added (over a period of 6 hr.) a solution of 15 g. (0.052 mole) of VII in 30 ml. of ether. After 15 hr. further refluxing, a solution of 15 ml. (0.16 mole) of purified[17] dimethyl sulfate in 60 ml. of benzene was added slowly. About half of the solvent was removed by distillation. The residue was refluxed 18 hr. longer and processed as per directions for 1-bromo-8-methylnaphthalene, crude yield 5.8 g. (50%) of liquid, b.p. 128–137° (0.35 mm.).

Further purification of the alkene was effected *via* the

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(14) Melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(15) A Lightnin Model 1 stirrer, equipped with a 2-inch stainless steel propeller with the blades inverted so as to force the liquid from top to bottom, was used. The stirrer and dropping funnel were positioned so as to prevent clotting of the reaction mixture and the excessive pastiness eventually resultant therefrom.

(16) F. Radt, *Elsevier's Encyclopaedia of Organic Chemistry,* Elsevier Publishing Company, Inc., New York, 1948, **12B**, (a) p. 388, (b) p. 390, (c) p. 831, (d) p. 372, (e) p. 293.

(17) L. F. Fieser, *Experiments in Organic Chemistry,* 2nd ed., D. C. Heath and Co., Boston, 1941, p. 373.

TNF molecular compound[18] (m.p. 105–135°), chromatographic dissociation thereof (using 1:1 by volume Celite-activated alumina as adsorbent and 30–60° petroleum ether as eluent), vacuum distillation, and conversion to the picrate, formed in methanol, recrystallized to constant m.p. (119–120°) from ethanol, obtained as orange-yellow needles (over-all yield 1.4 g., 6%).

Anal. Calcd. for $C_{23}H_{21}N_3O_7$: N, 9.31. Found: N, 9.43.

Chromatographic dissociation of the picrate by the preceding method gave colorless III, b.p. 108–109° (0.3 mm.).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 92.04; H, 8.30.

(*b*) *From 1-bromo-8-methylnaphthalene.* To the ice-cold Grignard reagent[7] prepared from 11.0 g. (0.050 mole) of 1-bromo-8-methylnaphthalene, 1.3 g. (0.054 g.-atom) of magnesium, 7 ml. of benzene, and 30 ml. of ether was added dropwise a solution of 5.4 g. (0.055 mole) of cyclohexanone in 8 ml. of benzene. Further processing followed the general directions of Bachmann and Kloetzel,[19] yield 3.4 g. (36%) of crude III, b.p. 148–155° (1 mm.). Treatment of this product with an equimolar quantity of TNF in glacial acetic acid and repeated crystallization (with occasional mechanical separation of some brown, high-melting by-product) from the same solvent gave red, silky needles of III.TNF molecular compound, m.p. 119–121° (over-all yield 7%).

1-(8-Methyl-1-naphthyl)cyclopentene (IV). To the Grignard reagent (at 10°) from 5.5 g. (0.23 g.-atom) of magnesium, 50 g. (0.23 mole) of 1-bromo-8-methylnaphthalene, 300 ml. of benzene, and 100 ml. of ether was slowly added a solution of 38 g. (0.45 mole) of cyclopentanone in 60 ml. of benzene. Further processing was conducted essentially as in the preparation of III, but with dehydration of the crude intermediate carbinol effected thermally (by heating at 200° in an atmosphere of nitrogen for 30 min.) instead of *via* anhydrous formic acid, yield 14.6 g. (30%) of yellow liquid, b.p. 130–140° (0.35 mm.). The product decolorized bromine in carbon tetrachloride and gave a positive Baeyer test.

For further purification a sample of the liquid was redistilled *in vacuo* from sodium (using a nitrogen bubbler) and converted to the picrate in absolute ethanol. Recrystallization thereof to constant m.p. (99–100°) from the same solvent produced orange needles.

Anal. Calcd. for $C_{22}H_{19}N_3O_7$: N, 9.61. Found: N, 9.68.

The purified alkene, recovered from the picrate by the method of Klemm and Hodes,[4] was obtained as a pale yellow liquid, b.p. 128–129° (0.6 mm.).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.84; H, 7.87.

5-Bromo-1-nitronaphthalene. To a stirred mixture of 500 g. (2.89 moles) of 1-nitronaphthalene and 5–6 g. of reduced (by hydrogen) iron powder, maintained at a temperature of 80–85°, was added dropwise over a period of 2–3 hr. 450 g. (2.81 moles) of bromine. About an hour later when gas evolution had ceased the reaction mixture was crystallized directly, once from ethanol and then once from acetone using Norit A both times, average yield 300 g. of fine yellow needles, m.p. 121–122°, plus 30 g. from processing of the mother liquors, m.p. 120–121° (47%, total); reported[16d] m.p. 122.5°.

5-Bromo-1-naphthylamine. To a vigorously stirred suspension of 168 g. (3 moles) of reduced (by hydrogen) iron powder in 1.25 l. of hot water was added 5 ml. of glacial acetic acid and then (cautiously in 20-g. portions and at such a rate as to maintain gentle reflux) 252 g. (1 mole) of 5-bromo-1-nitronaphthalene.

After an additional hour of heating and stirring, the mixture was cooled and the two phases were separated by decantation. The liquid phase was extracted once with ether; the solid phase, three times with hot acetone (filtered). Combined organic extracts were washed with excess 40% aqueous sodium hydroxide, dried (magnesium sulfate), concentrated *in vacuo* to a dark liquid, and extracted with 3.3 l. of boiling 0.33*N* hydrochloric acid. The gray-white needles of the amine hydrochloride which separated on cooling the extract were washed with 6*N* hydrochloric acid and air-dried. A sample of the hydrochloride was obtained almost pure white by recrystallization from dilute hydrochloric acid and then sublimation at 0.5–1.0 mm. pressure, m.p. > 225° (dec.).

The main part of the hydrochloride was suspended in ethanol and treated with an equivalent quantity of saturated aqueous potassium hydroxide. The precipitate which formed was removed by filtration and washed with ethanol. Combined filtrates were fractionally distilled, yield 117 g. (53%) of nearly white solid, b.p. 156–158° (1.4 mm. of nitrogen), m.p. 69–72°. A sample was recrystallized twice from 9:1 carbon tetrachloride-petroleum ether (60–90°), m.p. 69.5–71°; reported[20] m.p. 69°.

1-Bromo-5-iodonaphthalene. To a cooled, stirred solution of 155 g. (0.69 mole) of 5-bromo-1-naphthylamine in 1.4 l. of glacial acetic acid were added, at such a rate that the temperature did not exceed 20°, 37 ml. of concentrated sulfuric acid and then a solution of 55 g. (0.77 mole) of sodium nitrite in 550 ml. of concentrated sulfuric acid. When the intermediately formed precipitate had redissolved, 15 g. of urea was added. On cessation of evolution of gas the mixture was poured rapidly into a vigorously stirred solution of 170 g. (1.02 moles) of potassium iodide in 340 ml. of water. Again after evolution of gas had ceased, the mixture was heated to 90° for 30 min. and then poured slowly into a stirred solution of 120 g. of sodium bisulfite in 6 l. of water. The precipitate was collected from the cooled solution, dried, and distilled at 1.5 mm. pressure. The distillate boiling up to 175° was crystallized first from glacial acetic acid and then from acetone, yield 165 g. (72%) of needles, m.p. 118.5–120°; reported[21] yield 28%, m.p. 118°. Recrystallization of a sample from acetone (Norit A) gave m.p. 119–120°.

1-Bromo-5-methylnaphthalene. Following almost the exact procedure of Fieser and Seligman[7] for the preparation of the isomeric 1-bromo-8-methylnaphthalene there was obtained 15–21 g. (35–49%) of platelets (from methanol), m.p. 59.5–62°. Two recrystallizations from methanol raised the m.p. to 61–63°; reported[16e] m.p. 63–64°.

1-(5-Methyl-1-naphthyl)cyclohexene (V). The product, prepared as for III but in ether only, from interaction of the Grignard reagent of 1-bromo-5-methylnaphthalene (50 g.) and cyclohexanone (22 g.) was hydrolyzed and dehydrated (with anhydrous formic acid) by the procedure of Bachmann and Kloetzel.[19] Fractional distillation of the resultant alkene gave a crude yield of 28 g. (56%) of light yellow liquid, b.p. 137–142° (0.75 mm.). Treatment of a methanolic solution of the liquid with an equimolar amount of picric acid precipitated V-picrate, recrystallized from methanol to constant melting range 96–111°, yield 41 g. (41% over-all) of orange rods.

Anal. Calcd. for $C_{17}H_{18}\cdot C_6H_3N_3O_7$: picric acid, 50.8. Found:[22] picric acid, 51.2.

The picrate was dissociated chromatographically according to the method of Klemm and Ziffer[5] for TNB and TNF molecular compounds. Distillation of the effluent yielded colorless V, b.p. 153–154° (1.8 mm.).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.36; H, 8.30.

1-(5-Methyl-1-naphthyl)cyclopentene (VI). In a fashion analogous to the preparation of V, 100 g. of 1-bromo-5-methylnaphthalene yielded 52 g. (55%) of crude alkene, obtained as a yellow liquid, b.p. 135–145° (1 mm.) converted to VI.TNF[18] and recrystallized from glacial acetic acid to

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[18] L. H. Klemm, J. W. Sprague, and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

[19] W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **60**, 2204 (1938).

[20] F. Ullmann and F. Consonno, *Ber.*, **35**, 2802 (1902).

[21] G. Lock, *Monatsh.*, **81**, 850 (1950).

constant melting range 103–119°, yield 87 g. (37% over-all) of red needles.

Anal. Calcd. for $C_{16}H_{16}{\cdot}C_{13}H_5N_3O_7$: TNF, 60.2. Found:[22] TNF, 59.5.

Chromatographic dissociation of the molecular compound by the preceding method produced nearly colorless VI, b.p. 139–140° (1.4 mm.).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.83; H, 7.89.

EUGENE, ORE.

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[22] Determined spectrophotometrically by a procedure to be described elsewhere.

[CONTRIBUTION FROM THE POLYCHEMICALS RESEARCH DEPARTMENT, DOW CHEMICAL CO.]

Reaction of Ethylene Oxide with Urea

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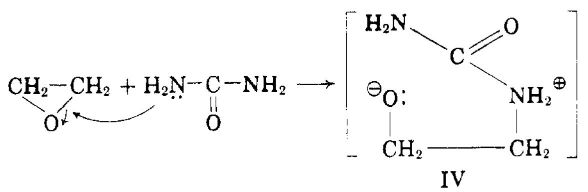
Received August 17, 1956

The reaction of equimolar amounts of ethylene oxide and urea gives as a main product β-aminoethylcarbamate, rather than the expected β-hydroxyethylurea. The reaction mechanism can be compared with an N → O acyl migration.

Pacquin[1] reported that a high molecular weight, water soluble product is obtained by reaction of ethylene oxide with urea at temperatures above 90°. However, the intermediates and the final product were ill defined.

The purpose of this paper is to present a study of the reaction products obtained by passing ethylene oxide into molten urea. It was shown that small amounts of β-hydroxyethylurea (I) and 2-oxazolidinone (II) were produced along with the main reaction product, β-aminoethylcarbamate (III).

The various products isolated and characterized in the experimental section are in conformity with a mechanism involving as a first step a nucleophilic attack by urea on ethylene oxide. This would give the transient intermediate (IV):

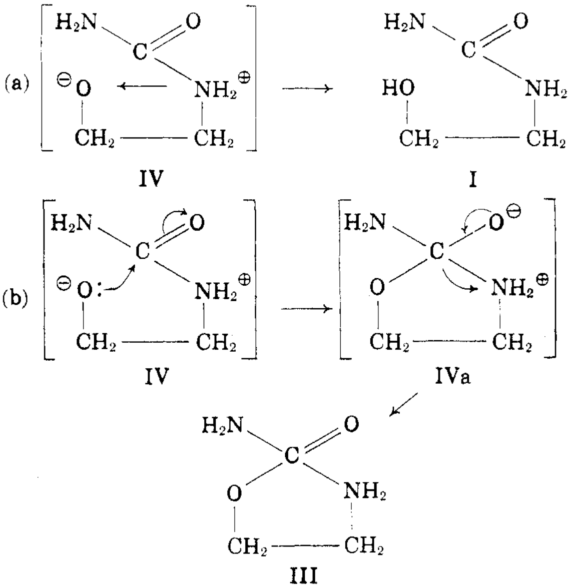


IV

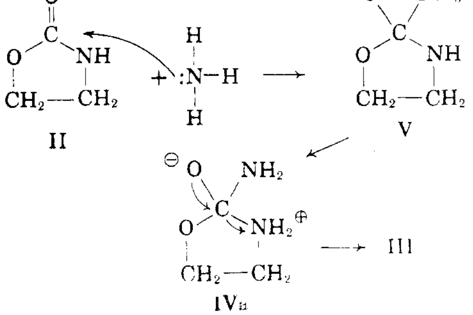
The intermediate could be stabilized by a proton transfer from nitrogen to oxygen to form β-hydroxyethylurea (I). An alternative method of stabilization could be an intramolecular nucleophilic attack of the negatively charged oxygen on the carbonyl carbon to form the cyclic intermediate (IVa), which subsequently dissociates into β-aminoethylcarbamate (III).

The latter mechanism is similar to that proposed by Van Tamelen[2,3] for the formation of *cis*-2-aminocyclopentyl (*p*-nitrobenzoate) by the action of hydrogen chloride on *cis* or *trans*-*N*-(*p*-nitrobenzoyl)-2-aminocyclopentanol.

The formation of 2-oxazolidinone (II) conceivably occurs by an elimination reaction involving the removal of ammonia from either (I) or (III). Close,[4,5] for example, converted β-hydroxyethylurea into 2-oxazolidinone by heating at 190–200°. By analogous treatment we were able to transform β-aminoethylcarbamate (III) into 2-oxazolidinone (II).



Finally it is of interest that 2-oxazolidinone (II) may be converted into β-aminoethylcarbamate



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[1] A. Pacquin, *Kunststoffe*, **37**, 165 (1947).

[2] Van Tamelen, *J. Am. Chem. Soc.* **73**, 5773 (1951).

[3] Van Tamelen, Tousignant, Peckham, *J. Am. Chem. Soc.* **75**, 1297 (1953).

[4] Close, *J. Am. Chem. Soc.* **73**, 95 (1951).

[5] Close, *J. Org. Chem.* **15**, 1131 (1951).