and extracted with 0.1 *N* sodium hydroxide. The organic layer was neutralized with 0.1 *N* hydrochloric acid, and chromatographed over alumina (grade III). Elution of the column with methanol afforded brownish needles of phenazine (33%) which recrystallized from ethanol as yellow needles, m.p. and mixture m.p. 171–171.5°.

The alkaline fraction was neutralized with 0.1 *N* hydrochloric acid and the precipitate isolated and recrystallized from acetone–water as yellow needles of phenazine-1-carboxylic acid (25%), m.p. and mixture m.p. 242–244°.

Phenazine-1-carboxamide (II) was prepared in 42% yield from phenazine-1-carboxylic acid according to the procedure of Kögl and Postowsky[19] employing thionyl chloride and ammonium hydroxide.

Acknowledgment.—This work was supported in part by Grant CA 06566 from the National Cancer Institute, U. S. Public Health Service.

[19] B. F. Kögl and J. J. Postowsky, *Ann.*, **480**, 280 (1930).

The Nef Reaction of 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophenanthrene

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Recently it was reported that 1,2,3,4,5,6,7,8,9,10,11,14 - dodecahydro - 9 - nitrophenanthrene (*1*) under Nef reaction conditions afforded a pair of isomeric ketones, 1,2,3,4,5,6,7,8,9,10,11,14-dodecahydro - 9 - ketophenanthrene (*2* and *3*, respectively, Fig. 1).[1] The conjugated ketone *3* also was obtained by heating the Nef ketone *2* in an acidic medium. The assignment of the position of the olefinic linkage in the conjugated ketone *3* was based on the ultraviolet spectral characteristics of both the α,β-unsaturated ketone and the 2,4-dinitrophenylhydrazone derivative. The absorption contants of the ketone *3* were reported to consist of maxima at 235 mμ (ϵ 3880) and 280 mμ (ϵ 940) in isoöctane.

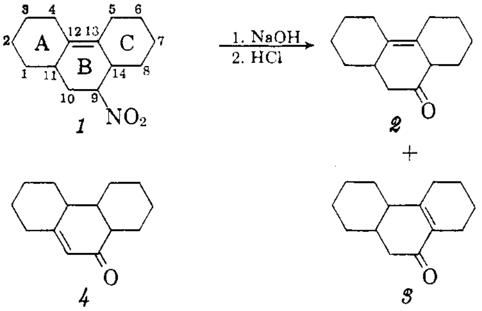

Figure 1

Interest in this problem was aroused when it was noted that the above maxima and extinction values were not consistent with structure *3*. In particular, the application of the usual correction factor for solvent change (isoöctane → ethanol, + 7 mμ) implied that the K-band for the ketone *3* was in the area of 242 mμ. A trisubstituted α,β-unsaturated ketone similar to *3* would be expected to absorb at about 247 mμ (Woodward's rules).[2] This discrepancy in the K-band's observed absorption maxima, as compared to the calculated value and the unusually low extinction sum, led to a reconsideration of the structure previously formulated for compound *3*. An interesting alternative to *3* was ketone *4* which was expected to possess an absorption around 240 mμ. If *4* was the correct structure for the conjugated ketone, then an abnormal reaction pathway must be invoked to rationalize the rearrangement of the double bond into the $\Delta^{10,11}$ position.

The nitro olefin *1* was resynthesized by a modification in the literature route. Specifically, bi-1-cyclohexen-1-yl was condensed with nitroethylene which was generated simultaneously *in situ* from 2-nitroethyl acetate and sodium acetate.[3] The well known disadvantages of pure nitroethylene were avoided by this indirect sequence. The presence of the double bond at $\Delta^{12,13}$ in compound *1* was assigned in the original work by ozonolysis experiments as well as by infrared arguments.

The n.m.r. spectrum of *1* revealed the proton on C-9 at 4.60 δ. This signal appeared to consist of a pair of doublets with couplings of 7 and 12 c.p.s., presumably due to spin-spin interaction with the two protons at C-10 as well as the proton at C-14. This information was used in an attempt to ascertain the preferred state of ring B and whether the nitro group existed in either the axial or equatorial configuration. If one assumed that the hydrogens C-11 and C-14 were *cis* to each other (*cis* addition *via* a Diels–Alder reaction) and were in the axial position, then the nitro group must be either in the axial or equatorial conformation. First, it may be said that any boat or half-boat form for ring B as visualized by Dreiding models appeared to be unstable and would collapse into the more rigid chair or half-chair form. More importantly, if the dihedral angles for the couplings between $J_{9,10}$ and $J_{9,14}$ were measured for the various axial or equatorial nitro configurations, then reference to the literature curve relating dihedral angle to $J_{H,H}{}'$ provided theoretical coupling values which were incompatible with the observed pattern.[4] Thus, the boat form of ring B was eliminated from further consideration.

Four possible chair or half-chair representations of ring B must be considered now. Number one of

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[1] N. L. Drake and C. M. Kraebel, *J. Org. Chem.*, **26**, 41 (1961).

[2] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," 2nd ed., Edward Arnold, Ltd., London, 1957, pp. 106, 107.

[3] H. Feuer, R. Miller, and C. B. Lawyer, *J. Org. Chem.*, **26**, 1357 (1961).

[4] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

the chair set had the nitro group axial and *trans* to the C_{14} proton; a coupling of about 3 c.p.s. was predicted here. The second example possessed the nitro group axial and *cis* to the C_{14} proton; a coupling constant of some 7 c.p.s. was visualized for this model. It appeared clear at this point that the axial configuration of the nitro group produced coupling sums far below the actual data. The third form contained an equatorial nitro which was *cis* to H_{14}. The dihedral angles were as follows: $\phi(H_{9a,14e}) = 180°$; $(H_{9a,10a}) = 175°$; and $(H_{9a,10e}) = 60°$. The equivalent theoretical couplings were therefore 10, 10, and 2 c.p.s., respectively. The total amounts to 22 c.p.s. and would give a pattern similar to the observed one. Experimental error in measuring the couplings and angles would account for the slight differences. The fourth and final state contained an equatorial nitro that was *trans* to H_{14}. The tabulated dihedral angles were found to be: $\phi(H_{9a,14a}) = 15°$; $(H_{9a,10a}) = 180°$; and $(H_{9a,10e}) = 60°$. The coupling constants would be 7, 10, and 2 c.p.s. Here, the sum is 19 c.p.s. and the actual pattern is not far from this predicted set. It was felt that both of the last two models fitted the real data; therefore, the only conclusion drawn was that ring B was in the chair or half-chair form and the nitro group was in the equatorial position.

An interesting phenomenon was noted in the n.m.r. spectrum in the area between 2.35 and 3.00 δ. One absorption was centered at 2.81 δ, whose integrated area was equivalent to one hydrogen, and a second peak was located at 2.62 δ with an area equal to two hydrogens. It was believed that the two equatorial protons located at C-8 and C-10 were shifted downfield by the long-range deshielding effects of the nitro group and thus appeared at lower field values than the allylic protons in compound *1*. The third proton was tentatively assigned as H_{14}, which is both allylic and near the nitro group and therefore was expected to appear even further downfield. The recognization of long-range shielding effects by the nitro group was noted only recently and may be of great importance to future structure proof work in alicylic nitro chemistry.[5]

The nitro olefin *1* was isomerized under Nef conditions to yield a mixture of β,γ-ketone *2* and α,β-ketone *3* (or *4*) as determined by infrared techniques. Gas chromatography of the crude product revealed that some starting nitro olefin *1* was still present as well as other unidentified materials. Various abortive efforts were made to separate and purify the two ketones by crystallization and liquid-solid chromatography. During an attempted vacuum distillation of *2* and *3* (or *4*), it was observed that compound *2* was being thermally isomerized into *3* (or *4*). A resulting slow evaporative distillation of the ketone mixture afforded an almost pure sample of *3* (or *4*). The ultraviolet spectrum of the α,β-unsaturated ketone in ethanol contained a maximum at 248 mμ (ε 12,470), which was completely consistent for structure *3*, but not for *4*. The n.m.r. spectrum contained no olefinic proton absorption and thereby confirmed the presence of a tetrasubstituted double bond in *3*. It was concluded that the previous spectroscopic properties associated with ketone *3* were in error and were due apparently to the low purity of the described compound. The new data obtained here fully support a direct isomerization of *2* into *3*.

In the latter stages of this work, a Communication appeared concerning the acid-catalyzed hydrolysis of 2-nitrooctane to 2-octanone.[6] Compound *1* was treated therefore with hydrochloric acid in various solvent combinations for extended periods of time. On work-up, the crude oil was shown to be a mixture of *1*, *2*, *3*, and other materials. No significant change in final product composition was observed in these experiments, as compared to the usual Nef sequence.

Experimental

Melting points were read on a Kofler block and are not corrected; boiling points are uncorrected, also. The ultraviolet spectra (recorded in mμ) were obtained in ethanol, unless otherwise stated, on a Cary Model 14 recording spectrophotometer. Infrared spectra (recorded in μ) were determined in pressed potassium bromide disks or as neat films using a Perkin-Elmer Model 421 double beam grating instrument. Isothermal gas–liquid chromatograms were measured on the Wilkens Instrument A-600 and the A-90 devices. Thin-layer chromatoplates were coated with Merck (Darmstadt) silica gel containing calcium sulfate as a binder. Ceric sulfate was utilized as a visualization agent. All n.m.r. measurements were conducted in deuterochloroform solution using tetramethylsilane as an internal reference on the Varian Associates A-60 machine. Proton n.m.r. signals were noted in p.p.m. as δ-values [c.p.s. (relative to tetramethylsilane)/60]. The microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, Stanford University.

Bicyclohexyl-1,1′-diol.—The bimolecular reduction of cyclohexanone with aluminum amalgam gave consistent 33–35% yields of the desired compound. The diol melted at 123.0–124.0° [lit.,[7] 123–124°] and exhibited $\lambda\lambda_{max}$ 2.93 (hydroxyl) and 10.38 (cyclohexyl).

Bi-1-cyclohexen-1-yl.—The diene was produced by the dehydration of bicyclohexyl-1,1′-diol in 80–82% yields by use of phosphorus oxychloride and pyridine.[8] The material was a colorless oil which boiled at 48.4–49.3° (0.09 mm.) [lit.,[7] b.p. 95–96° (3 mm.)] and gave a single peak on gas phase chromatography using a 20% SE-30 on a base-washed Chromosorb P column at 173°; thin-layer chromatography showed a single peak at the solvent front with ether–benzene (1:4) as the eluant. The diene exhibited $\lambda\lambda_{max}$ 232 (shoulder) (log ε 4.18), 238 (log ε 4.23), and 245 (shoulder) (log ε 4.11) [lit.,[9] $\lambda\lambda_{max}^{n\text{-hexane}}$ 231 (log ε 4.25) and 238 (log ε 4.26)]; $\lambda\lambda_{max}^{film}$ 3.30 (aliphatic olefin) and 12.55 (trisubstituted olefin); and $n^{25}\text{D}$ 1.5341. Occasionally, the diene crystallized on standing in the cooler night air to afford long, colorless needles that melted at about 26°.

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(5) A. C. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962).

(6) H. Feuer and A. T. Nielsen, *J. Am. Chem. Soc.*, **84**, 688 (1962).

(7) I. Nazarov and I. Torgov, *Zh. Obshch. Khim.*, **22**, 228 (1952).

(8) D. Greidinger and D. Ginsburg, *J. Org. Chem.*, **22**, 1406 (1957).

(9) G. Laber, *Ann.*, **588**, 79 (1954).

2-Nitroethanol.—This material was purchased from Columbia Organic Chemicals, Columbia, S. C.

2-Nitroethyl Acetate.—The acetate was prepared by sulfuric acid-catalyzed esterification with acetic anhydride.[10a,b] The ester boiled at 68–69° (1.2 mm.) [lit.,[10b] b.p. 62–64° (1.3 mm.)]; yield, 83–85%. The compound possessed $\lambda\lambda_{max}^{film}$ 5.72 (carbonyl), 6.40 and 6.92 (nitro), and 8.10 (acetate).

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophanenthrene (*1*).—In a typical preparation, 2-nitroethyl acetate (19.6 g., 0.148 mole) was added dropwise over a 30-min. period to a stirred suspension of sodium acetate (12.4 g., 0.150 mole) and a solution of bi-1-cyclohexen-1-yl (24.0 g., 0.148 mole) in benzene (155 ml.). Afterwards, the two-phase mixture was refluxed for 16 hr.; previous model experiments had shown that a maximum yield was obtained at the end of this period. The cooled reaction mixture was filtered through a sintered funnel and the inorganic salts were washed with hot benzene (2 × 10 ml.). The combined organic phases were treated with Norit, were refiltered, and were evaporated to dryness *in vacuo* to leave a red oil. This material was twice crystallized from alcohol and then was sublimed readily at 60° (0.1 mm.); yield, 14.2 g. (40.9%); m.p. 72.5–73.4° (lit.,[1] m.p. 74.0–74.8°); the solid produced a single peak on gas phase chromatography using a 20% SE-30 on an acid-washed Chromosorb P column at 178°; thin-layer chromatography showed a single spot near the solvent front with pentane as the eluent. The nitro olefin exhibited no selective absorption in the ultraviolet above 210 mμ; $\lambda\lambda_{max}$ 3.41 and 3.51 (aliphatic olefin), 6.52 and 7.25 (nitro), and 12.95 (ring methylene). The n.m.r. spectrum contained signals centered at 4.60 (the hydrogen attached to the carbon holding the nitro group), 2.80 and 2.60 (integrated area equivalent to one and two hydrogens, respectively), and a series of overlapping peaks stretching from 1.98 to 1.47 (miscellaneous aliphatic hydrogens).

Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.48; H, 9.15; N, 5.73.

1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-9-ketophenanthrene (*3*).—A cold solution of sodium hydroxide (5.00 g., 0.125 mole) in ethanol (100 ml.) was slowly added to a chilled stirred solution of nitro olefin *1* (10.9 g., 0.0424 mole) in ethanol (100 ml.). The combined liquids were held at 0–2° under a nitrogen atmosphere for 30 min. and were then poured into a cold, dilute hydrochloric acid solution (2 *N*, 300 ml.). The resulting mixture was stirred at 5° for 2 hr. and was allowed to warm to room temperature over a day. The organic material was extracted with ether (3 × 300 ml.) and the combined extracts were dried over magnesium sulfate and were taken to dryness *in vacuo* to leave a brown oil, wt. 9.5 g. Thin-layer chromatography with benzene as the eluent revealed the presence of four components. The infrared spectrum exhibited two carbonyl bands—5.85 (β,γ-ketone *2*) and 6.01 (α,β-ketone *3*); some starting material was noted, also (6.49 and 7.25). Gas phase chromatography using a silicone rubber on an acid-washed Firebrick column at 150° produced four separable peaks: unknown material, β,γ-ketone *2*, α,β-ketone *3*, and nitro olefin *1*. It was not possible to separate the two ketones by column chromatography with silicic acid and petroleum ether.

An effort to distil the ketone mixture revealed that the application of heat was isomerizing compound *2* into the desired *3*; therefore, the impure brown oil (1.0 g.) was distilled slowly at 70° (0.12 mm.) to yield a pale yellow oil (0.46 g.). This latter product gave a major peak (95%) and a minor, trailing peak (5%) on gas phase chromatography using a 20% SE-30 on an acid-washed Chromosorb P column at 202°; thin-layer chromatography showed a single spot with benzene as the eluent; λ_{max} 248 (log ε 4.09); $\lambda\lambda_{max}^{film}$ 6.03 (carbonyl) and 6.19 (double bond); and n^{23}_D 1.5472. The n.m.r. spectrum did not contain any olefinic proton absorptions. The physical constants of *3* were not further improved by preparative gas chromatography.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.10; H, 9.82.

The brilliant red 2,4-dinitrophenylhydrazone was crystallized from ethyl acetate–grain alcohol (1:1) and then from ethanol; m.p. 231.0–231.5° (lit.,[1] 233.5–234.1°); $\lambda\lambda_{max}^{CHCl_3}$ 258 (log ε 4.25), 290 (shoulder) (log ε 3.42), and 393 (log ε 4.46 [lit.,[1] $\lambda\lambda_{max}^{CHCl_3}$ 260 (log ε 4.31) and 293 (inflection)].

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.46; H, 6.36; N, 14.58.

The white semicarbazone was crystallized from methanol-ether (1:1), m.p. 181.5–182.0°; $\lambda_{max}^{CH_3OH}$ 268 (log ε 4.52).

Anal. Calcd. for $C_{15}H_{23}N_3O$: C, 68.93; H, 8.87; N, 16.08. Found: C, 68.66; H, 9.05; N, 15.80.

Acid Hydrolysis of 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophenanthrene.—The nitro olefin *1* (0.253 g., 0.0011 mole) was refluxed with grain alcohol (100 ml.) containing concentrated hydrochloric acid (0.20 ml.) for 15 days. The solvent was removed *in vacuo* to afford a brown oil which was analyzed by gas chromatography using a 5% SE-30 on an acid-washed Chromosorb W column at 212°. The composition of the crude product was as follows (arranged in order of increasing retention time): other products (4%), β,γ-ketone (30%), α,β-ketone (25%), and starting material (41%).

A second reaction involved nitro olefin (0.520 g., 0.0022 mole) and a mixture of ethanol (80 ml.) and dilute hydrochloric acid (1 *N*, 170 ml.) which was boiled for 12 days. Work-up of the crude oil produced a similar result: unknown materials (8%), β,γ-ketone (41%), α,β-ketone (33%), and starting compound (18%).

Finally, nitro olefin (0.520 g.) was heated with dilute hydrochloric acid (1 *N*, 250 ml.) for 15 days. The oil (0.283 g.) was comprised of other compounds (5%), β,γ-ketone (40%), α,β-ketone (35%), and nitro olefin (20%).

Acknowledgment.—The authors are indebted to Mrs. Dalia Aguilar for the infrared and ultraviolet absorption spectra, to Dr. Lois J. Durham for discussions concerning the n.m.r. data, and to Mr. Erich H. Meier for the microanalyses.

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The Synthesis of (+)-3-Methyl-β-citronellal

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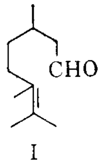
The synthesis of DL-3-methyl-β-citronellal (DL-V) has been accomplished[1] by the selective hydrogen-



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