Rearrangements of 5-Nitronorbornenes. II. 6-Phenyl- and 6-Methyl-5-nitro-2-norbornenes

WAYLAND E. NOLAND, RICHARD B. HART,[1a] WILLIAM A. JOERN,[1b] AND R. GERALD SIMON[1c]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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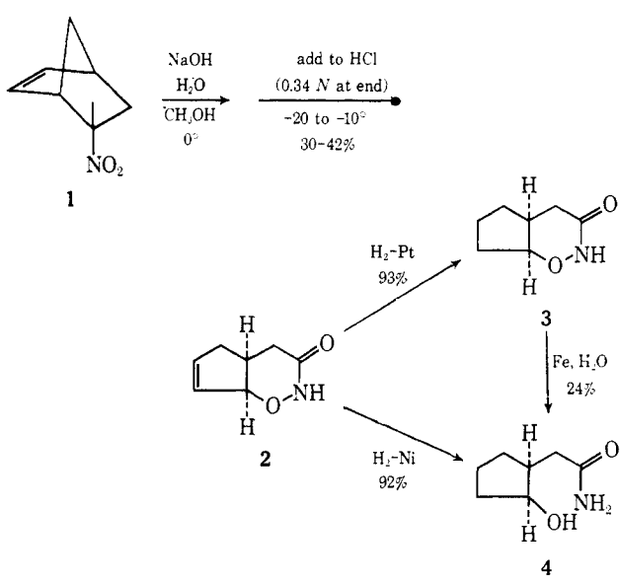
Rearrangement of the salts of 6-phenyl- (**5a**) and 6-methyl-5-nitro-2-norbornenes (**5b**) in aqueous methanolic hydrochloric acid gave isomeric rearrangement products **6a** and **6b**. Hydrogenation of **6a** and **6b** over platinum gave dihydro derivatives **9a** and **9b** and over Raney nickel gave dihydrodeoxo derivatives **12a** and **12b**, the hydrogenolysis in the latter cases supporting the assignment of hydroxamide structures to **6a** and **6b**. Ozonolysis of **6a** to the known 1-phenylpropane-1,2,3-tricarboxylic acid (**19**), and an independent synthesis of the 3 epimer (**17**) of the dihydrodeoxo derivative (**12a**) of **6a**, established the structure of **6a** as 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one. By analogy the corresponding 3-methyl structure is assigned to **6b**. The lactam structure of **12a** was extremely resistant to acidic hydrolysis or reduction with $LiAlH_4$, but epimerized (to **17**), particularly under alkaline conditions, whereas **12b** did not epimerize, but was readily hydrolyzed (to amino acid hydrochloride **41**) and reduced with $LiAlH_4$ to the amine, 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-methylcyclopenta[*b*]pyrrole (**42**). The mechanism of formation of the rearrangement products is discussed.

It has been shown previously in this laboratory that the product of rearrangement under acidic conditions of the sodium salt of 5-nitro-2-norbornene (**1**) is 2,3,4,4a-*cis*-5,7a-*cis*-hexahydrocyclopenta[*e*]-1,2-oxazin-3-one (**2**).[2] Two key degradation products, of interest in the discussion which follows, are the dihydro derivative (**3**), derived from hydrogenation over platinum, and the tetrahydro derivative (**4**), derived from hydrogenation over Raney nickel. In order to determine the effect of substitution on the rearrangement, we have now subjected the salts of the 6-phenyl (**5a**) and 6-methyl (**5b**) derivatives of **1**, which, like **1**, are available from the Diels–Alder reaction of cyclopentadiene with the appropriate nitroolefins, to the acidic rearrangement.

Phenyl Rearrangement Product (6a).—Rearrangement of the sodium or potassium salt of the 6-phenyl derivative (**5a**) in aqueous methanolic hydrochloric acid gave a crystalline product (**6a**), isomeric with the starting material, in yields as high as 43–57%. The transformations **6a** → **18** shown in Scheme I,[3] and the additional data included in the Experimental Section, are consistent with the assignment to **6a** of a hydroxamide structure [–C(=O)N(OH)–], in contrast to the cyclic hydroxamate structure established for **2**.



Ozonolysis of the phenyl rearrangement product (**6a**) at −78° in methanol, followed by oxidative work-up with performic acid, gave in 55% yield a key degradation product, the known 1-phenylpropane-1,2,3-tricarboxylic acid (**19**), identical with a synthetic sample prepared *via* sodium ethoxide catalyzed condensation of mandelonitrile with ethyl cyanoacetate, and then with ethyl chloroacetate, according to the procedure of Chatterjee and Barpujari.[4]

Among the most likely structures for the phenyl rearrangement product are **6a**, **20a**, **21a**, and **22**. If the intermediate nitronic acid of **5a** is considered as the N-oxide of an oxime, which might undergo a Beckmann-type rearrangement, then structures **20a** and **21a** are potentially derivable from migration of the 4 and 6 carbons of **5a**, respectively, to nitrogen. Structure **20a** is also derivable by a ring reclosure reaction, as will be discussed later in the Mechanism Section. Structure **22** is the phenyl-substituted analog of the unsubstituted rearrangement product[2] (**2**), and is potentially derivable in a manner completely analogous to that of **2** by a ring reclosure reaction through oxygen acting as the nucleophile. Structure **6a** is potentially derivable by an analogous ring reclosure reaction through nitrogen rather than oxygen acting as the nucleophile. Structure **22**, although consistent with the ozonolysis product, can be eliminated immediately because it is not a hydroxamide, would not give a positive ferric chloride test, and, by analogy with **2** (which gave a tetrahydro derivative), would not be expected to give a dihydrodeoxo (or deoxo) derivative. The hydroxamide structure **21a** can be eliminated because, with a nitrogen

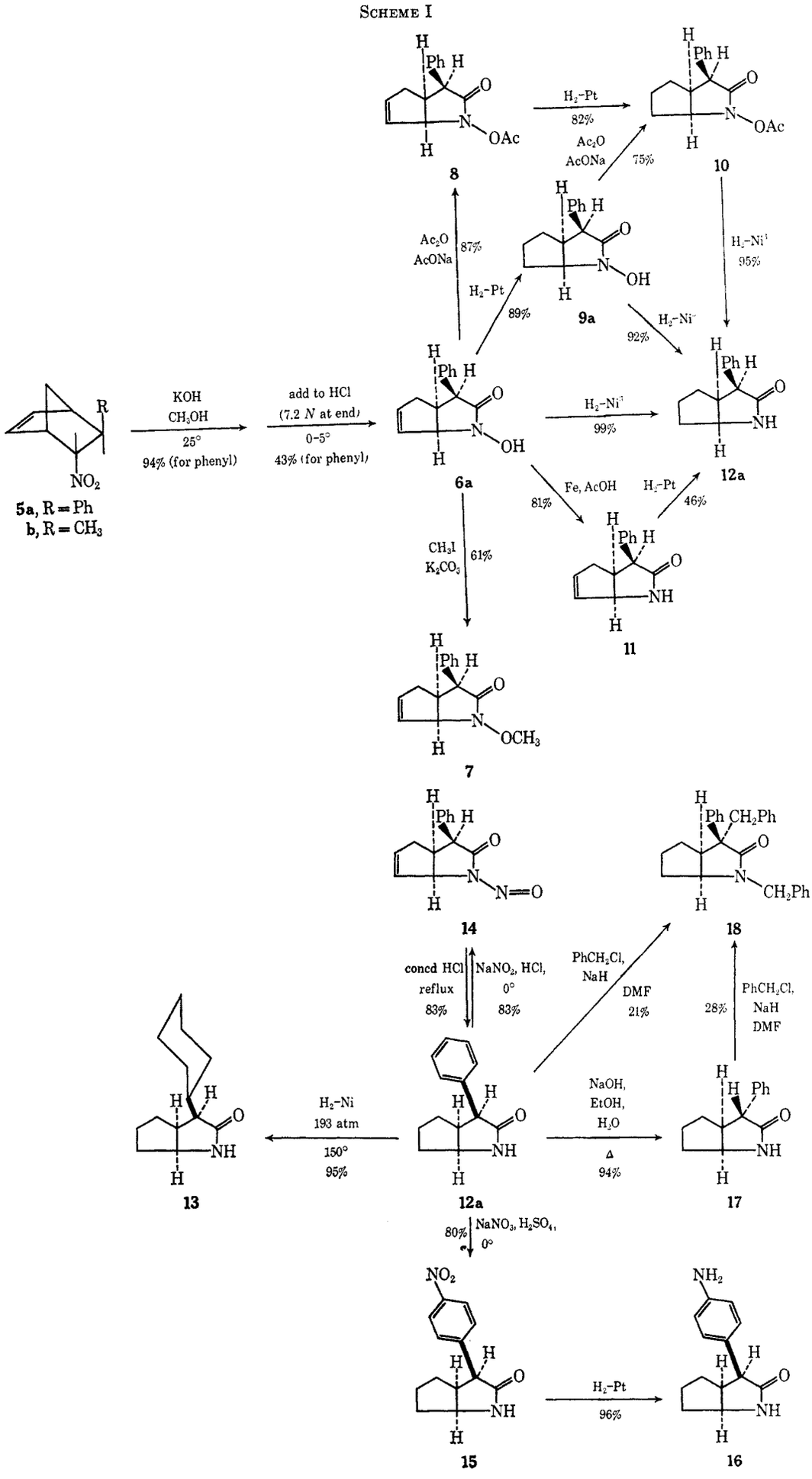
(1) (a) Taken in large part from the Ph.D. thesis of Richard B. Hart, University of Minnesota, August 1964; *Dissertation Abstr.*, **26**, 695 (1965). It is a pleasure to acknowledge support of much of this work through fellowships to R. B. H. from the George Macpherson Fellowship of the Graduate School of the University of Minnesota (academic year 1962–1963), the Sun Oil Co. Fellowship (academic year 1963–1964), the National Science Foundation Summer Fellowships (summers of 1962, 1963, and 1964), and the Monsanto Co. (second summer session 1961); taken in part from initial exploratory studies by (b) William A. Joern, M.S. degree research, University of Minnesota, 1959–1960; and (c) R. Gerald Simon, research, University of Minnesota, Jan–Feb 1961.

(2) (a) Paper I: W. E. Noland, J. H. Cooley, and P. A. McVeigh, *J. Amer. Chem. Soc.*, **81**, 1209 (1959); (b) *ibid.*, **79**, 2976 (1957).

(3) Hydrogenolysis of hydroxamides and alkoxamides over Raney nickel at low pressure is well known. For numerous illustrations see, for example, W. E. Noland and R. J. Sundberg, *J. Org. Chem.*, **28**, 3150 (1963); *Tetrahedron Lett.*, 295 (1962).

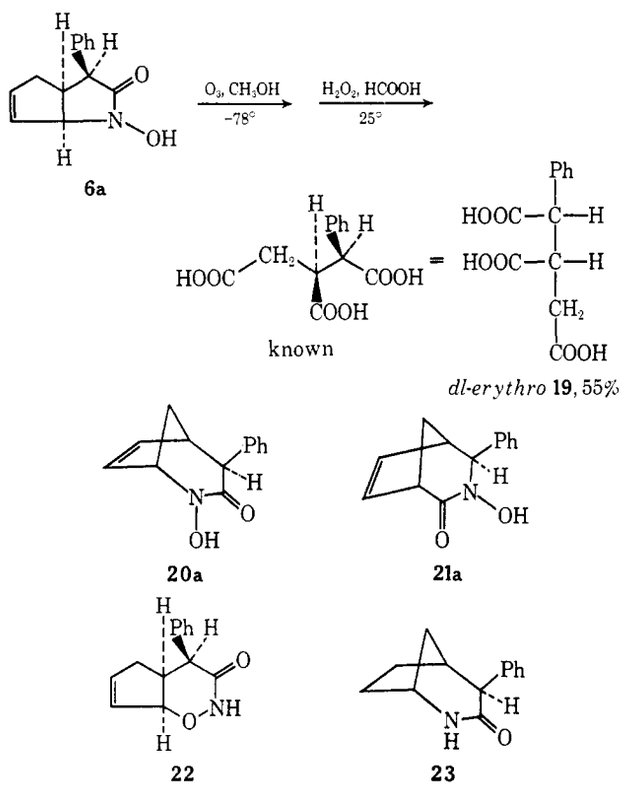
(4) N. N. Chatterjee and G. N. Barpujari, *J. Indian Chem. Soc.*, **17**, 292 (1940).

SCHEME I


5a, R = Ph
b, R = CH3
KOH
CH3OH
25°
94% (for phenyl)
add to HCl
(7.2 N at end)
0-5°
43% (for phenyl)
6a
8
10
9a
12a
11
7
14
18
13
15
16
17
H2-Pt
82%
Ac2O
AcONa
75%
Ac2O
AcONa
87%
H2-Pt
89%
H2-Ni
95%
H2-Ni
92%
H2-Ni
99%
Fe, AcOH
81%
H2-Pt
46%
CH3I
K2CO3
61%
concd HCl
reflux
83%
NaNO2, HCl,
0°
83%
PhCH2Cl,
NaH
DMF
21%
PhCH2Cl,
NaH
DMF
28%
H2-Ni
193 atm
150°
95%
NaOH,
EtOH,
H2O
Δ
94%
80%
NaNO3, H2SO4,
0°
H2-Pt
96%

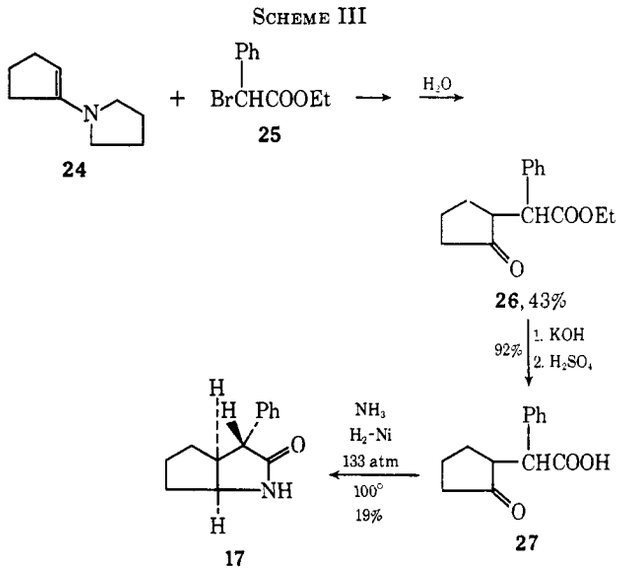
rather than a carbonyl attached to the benzyl carbon, it could not give rise to the substituted phenylacetic acid structure present in the ozonolysis product. The hydroxamide structures **6a** and **20a** are consistent with the ozonolysis product, and with the epimerization and benzylation data, which seem to require that the phenyl substituent be on a carbon α to a carbonyl group for the necessary enolate anion to form (Scheme II). Efforts were then directed toward differentiating between the two possible structures (**6a** and **20a**) for the phenyl rearrangement product.

SCHEME II



Because of the complex functionality of the rearrangement product, efforts were directed toward independent syntheses of the simpler dihydrodeoxo derivatives **12a** and **23**[5] derivable from **6a** and **20a**. Synthesis of the epimer (**17**) of the dihydrodeoxo derivative **12a** was accomplished from the pyrrolidine enamine of cyclopentanone (**24**), as shown in Scheme III. The product (**17**, mp 128.5–129.5°) was different from the dihydrodeoxo derivative (**12a**, mp 171–172°) and, although it had the proper melting point, it was also first thought to be different from epimer **17** because of substantial differences in the infrared spectra in Nujol.[1a] These differences led to the incorrect formulation of the phenyl rearrangement product (**6a**) and its derivatives (**7–18**) in the Hart thesis[1a] as the alternate structure **20a** and its corresponding derivatives (including **23**). Hart found subsequently, however, that the nmr spectra of the two samples of **17** in chloroform-*d* were identical, and that the differences in the Nujol infrared spectra were attributable to the existence of dimorphic forms, both of which were isolated at various times from epimerization of the dihydrodeoxo derivative (see the Experimental Section). Thus it follows that the dihydrodeoxo derivative has structure **12a** and its precursor, the phenyl rearrangement product, must have structure **6a**.

SCHEME III



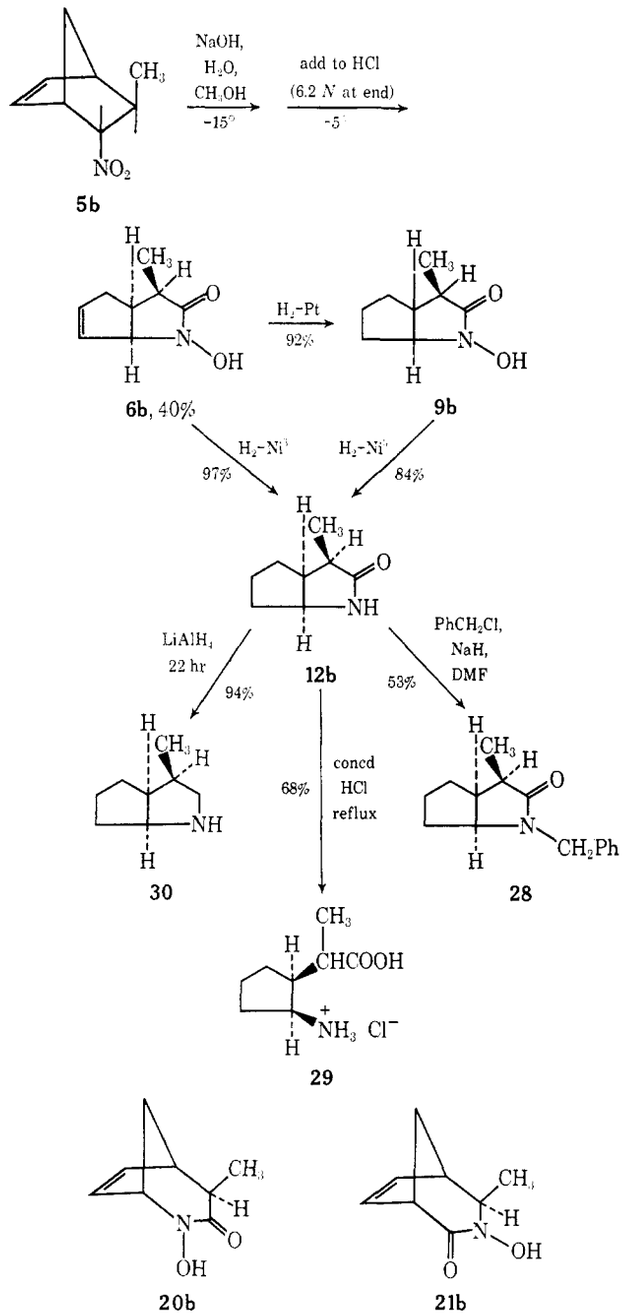
Methyl Rearrangement Product (**6b**).—Rearrangement of the sodium salt of 6-methyl-5-nitro-2-norbornene (**5b**) in aqueous methanolic hydrochloric acid also gave a crystalline product (**6b**), isomeric with the starting material, in 40% yield. The transformations **6b** → **30** shown in Scheme IV, and the bright purple ferric chloride tests given by **6b** and **9b** (like **6a** and **9a**), show that **6b** has a hydroxamide structure like the phenyl rearrangement product (**6a**). The methyl dihydrodeoxo derivative **12b**, having a less acidic hydrogen α to the carbonyl group, does not epimerize or undergo C benzylation under the basic conditions where the phenyl derivative **12a** does. Also in contrast to **12a**, in which the phenyl substituent sterically prevents hydrolysis or hydride reduction at the carbonyl group, **12b** hydrolyzed in refluxing concentrated hydrochloric acid to the amino acid hydrochloride **29**, and reduced with lithium aluminum hydride to the cyclic secondary amine **30**.

By analogy with structure **6a** established for the phenyl rearrangement product, the methyl rearrangement product is assigned structure **6b** rather than the alternative hydroxamide structures **20b** and **21b** (analogous to **20a** and **21a**), although all three structures are consistent with the chemical data presented.

Effect of Reaction Conditions.—The rearrangement product (**2**) from 5-nitro-2-norbornene (**1**) was obtained under milder conditions of acidity (2.6 *N* HCl at the start and 0.3 *N* at the end) than the rearrangement products **6a** (from the 6-phenyl derivative **5a**; 12 *N* HCl at the start and 7.2 *N* at the end) and **6b** (from the 6-methyl derivative **5b**; 12 *N* HCl at the start and 6.2 *N* at the end), which were isolated under similar conditions. Developmental work[1b,c] carried out on the rearrangement of the salt of the 6-phenyl derivative (**5a**) showed that the reaction is favored by (1) high acid concentration (6–12 *N* HCl), (2) slow addition of the salt solution to the acid, (3) the presence of methanol as a solubilizing agent, (4) probably by reaction temperatures in the range of 0–10°, and (5) use of freshly prepared salt. The latter factor is probably

(5) Four unsuccessful approches to the synthesis of the alternate structure **23** are described in the Hart thesis.[1a]

SCHEME IV



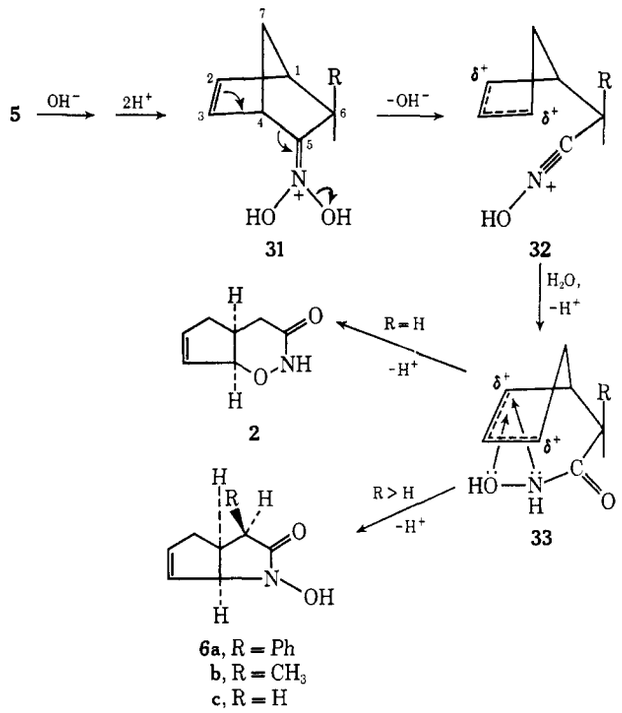
favored because of a slow autoxidation of the nitro compound salt to nitrite,[6] which otherwise probably leads during the acidification to increased amounts of nitrosation by-products (such as pseudonitroles).

Mechanism.—The mechanism previously proposed[2] to account for formation of the unsubstituted rearrangement product (**2**) can be adapted to account for all three rearrangement products. The mechanism probably proceeds through the doubly protonated nitronate anion (**31**), the conjugate acid of the nitronic acid, which undergoes ring opening and elimination of hydroxide ion to give an allylic carbonium ion–nitrile oxide, or its conjugate acid (**32**) (Scheme V). Cristol and Freeman[7] have reported a ring fission reaction of 5-norbornen-2-one (**34**) with sodium amide or potassium

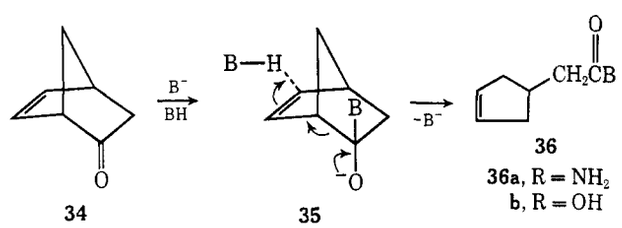
(6) (a) G. A. Russell, *J. Amer. Chem. Soc.*, **76**, 1595 (1954). (b) For additional examples, see W. E. Noland, *Chem. Rev.*, **55**, 137 (1955).

(7) S. J. Cristol and P. K. Freeman, *J. Amer. Chem. Soc.*, **83**, 4427 (1961).

SCHEME V



t-butoxide to give 3-cyclopentene-1-acetamide (**36a**) or 3-cyclopentene-1-acetic acid (**36b**) in which, as they have noted, the electron flow (**35**) is just the reverse of that which we have postulated[2] for the ring-fission process **31** → **32**.



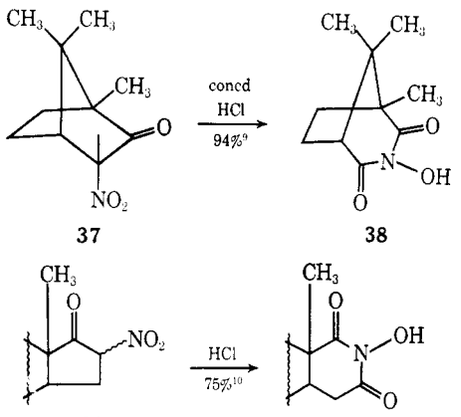
Hydrolysis of the protonated nitrile oxide (**32**) should give the corresponding hydroxamic acid (**33**). This intermediate could then react along one of several subsequent pathways, depending on steric and possibly electronic factors.

One possible reaction pathway (type 1 rearrangement), which has not so far been observed when an alternate pathway is present (as in our examples), would be nucleophilic attack by the hydroxamic nitrogen on the same (now positive) carbon from which the original ring fission occurred. In our examples this would be the allylic, original C-4 bridgehead carbon in **5**. This pathway would regenerate a bicyclic system, giving one (**20a**, **20b**) of the two types of hydroxamide suggested earlier also as possible products of a Beckmann-type rearrangement. The type 1 rearrangement has been observed in the acid-catalyzed rearrangements of the α-nitro ketones 3-*endo*-nitro-2-bornanone[8] (**37**) and 3β-hydroxy-16-nitroandrost-5-en-17-one (**39**, a 1:1 mixture of the 16α- and 16β-nitro epimers) and its 5,6-dihydro derivative, which have been shown to give N-hydroxycamphorimide[9] (**38**) and 3β,N-dihydroxy-16,17-secoandrost-5-ene-16,17-dioic imide (**40**) and its 5,6-

(8) A. A. Griswold and P. S. Starcher, *J. Org. Chem.*, **30**, 1687 (1965).

(9) H. O. Larson and E. K. W. Wat, *J. Amer. Chem. Soc.*, **85**, 827 (1963).

dihydro derivative,[10] respectively. Hassner and Larkin[10] have suggested that these rearrangements may also proceed through cleavage to a nitrile oxide (analogous to **32**) and thence to a hydroxamic acid intermediate (analogous to **33**). In these examples, the acidity of the hydrogen α to both the carbonyl and nitro groups is sufficiently great that it is not necessary, as in our examples, to first form the salt in order to generate the nitronic acid upon acidification; with the α-nitro ketones the nitronic acid must form directly by acid-catalyzed enolization. The rearrangements also proceed with benzoyl chloride under Schotten–Baumann reaction conditions, giving the benzoate of **38**,[9] and with acetic anhydride, giving the 3β,N-diacetate of **40** or its 5,6-dihydro derivative.[10] Hassner and Larkin[10] have made the plausible suggestion that these examples may also proceed through the nitrile oxide mechanism, in which an acyl group replaces a proton as catalyst and an anhydride molecule (or more probably an acylate ion or its conjugate acid) replaces a water molecule as a co-catalyst. The opposite type of ring closure reaction to the type 1 rearrangement to form bicyclic systems, in which a nucleophilic center (double bond) *in a ring* attacks an *exocyclic* electrophilic center, has been studied extensively by Bartlett and coworkers.[11]



A second possible reaction pathway (type 2 rearrangement), which is observed in our examples, involves ring closure through nucleophilic attack at the other end of the allylic carbonium ion system, at the original C-2 vinyl carbon in **5**. Thus, ring closure through the hydroxamic oxygen (type 2a rearrangement) would give the hydroxamate type of structure (**22**) previously observed[2] (**2**) in the unsubstituted case. This reaction pathway was not observed when the 6-*exo*-phenyl[12] (**5a**) or methyl (**5b**) substituents are present in **5**, as the products (**6a**, **6b**) are hydroxamides. Instead, for reasons which may relate to protonation of the oxygen in the more strongly acidic media employed,[13] ring closure occurs in the corresponding fashion, but through nitrogen (type 2b rearrangement) rather than oxygen, giving 5:5 fused ring products (**6a**, **6b**). Since the yields of rearrangement products (43–57% of **6a**, and 40% of **6b**) exceeded the amounts of 5-*exo*-nitro-6-*endo*-substituted minor stereoisomers present in the starting mixtures,[12] the products must be derived from the major stereoisomers **5a** and **5b**. It follows from the mechanism proposed that the 6-*exo* substituents in **5a** and **5b** become the 3-substituents in **6a**[14] and **6b** and their derivatives and remain *trans* to the 3a-hydrogen at the adjacent ring junction. Thus, epimerization of the dihydrodeoxo derivative **12a** to **17** relieves the serious *peri*-1,3-steric interaction between the inward-pointing 3-phenyl and 4-hydrogen substituents in **12a**.[15,16]

Experimental Section

Melting points were determined on calibrated hot stages. Ultraviolet spectra were determined on Bausch and Lomb Spectronic 505 or Cary Model 11 recording spectrophotometers. Infrared spectra were determined on Beckman IR5, Perkin-Elmer 21, or Unicam SP-200 spectrophotometers. Nuclear magnetic resonance (nmr) spectra were determined on a Varian A-60 spectrometer. Microanalyses were performed largely at the University of Minnesota by Mrs. Olga Hamerston and Dr. T. S. Prokopov and their assistants, particularly Mrs. Kathleen Nelson Juneau and Lawrence L. Landucci, and at the Scandinavian Microanalytical Laboratory in Herlev, Denmark.

The Potassium Salt of 5-Nitro-6-phenyl-2-norbornene.—5-Nitro-6-phenyl-2-norbornene[17] (60.0 g, 0.279 mol) was added dropwise with vigorous stirring at room temperature to a solution of potassium hydroxide (17.3 g, 0.308 mol) in methanol (300 ml). The resulting yellow solution was stirred for 12 hr. Then the methanol was removed carefully in a rotary evaporator, keeping the temperature below 40°, leaving a red gummy residue. This residue was cooled and washed with ether–acetone (>3:1, 200–300 ml) at 0°, causing formation of a yellowish white solid (66.4 g, 94%): ν_{max}^{Nujol} (cm^{-1}) 3280 and 3140 (m, OH), 1615 (s, C=N), 1590 (ms, C=C). The solid was insoluble in ether but somewhat soluble in water. It was used in the next step without further purification.

Rearrangement of the Salt of 5-Nitro-6-phenyl-2-norbornene in Aqueous Methanolic Hydrochloric Acid. 1,2,3-*cis*-3a-*cis*-Hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (6a).—A solution of the potassium salt of 5-nitro-6-phenyl-2-norbornene (89.0 g, 0.351 mol) in water (200 ml) and methanol (300 ml) at 0° was added dropwise with vigorous stirring over 2 hr to concentrated hydrochloric acid (800 ml, 9.60 mol) cooled to 0° in an ice–salt bath, never allowing the temperature to rise above 5°. During the addition, the reaction solution became opaque and light blue-green, and a considerable amount of blue-green oil formed,

(10) A. Hassner and J. Larkin, *J. Amer. Chem Soc.*, **85**, 2181 (1963).

(11) (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (b) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (c) P. D. Bartlett, W. S. Trahanofsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965).

(12) W. E. Noland, B. A. Langager, J. W. Manthey, A. G. Zacchei, D. L. Petrak, and G. L. Eian, *Can. J. Chem.*, **45**, 2969 (1967).

(13) The type of rearrangement product formed (such as **22** or **20**) may depend on the conditions of acidity employed. As noted in the section on Effect of Reaction Conditions, product **2** was isolated previously[2] under markedly lower conditions of acidity than **6a** or **6b**. It has recently been shown also that **2** is the crystalline product (isolated in 25% yield) from rearrangement of the sodium salt of **1** under higher conditions of acidity (12 *N* HCl at the start and 3.3 *N* at the end) than used previously in the isolation of **2**: John M. Olson, senior thesis research, University of Minnesota, fall 1967, NSF Undergraduate Academic Year Research Participant. From the sodium salt of **1** under conditions of acidity the same as those used in the isolation of **6a** (12 *N* HCl at the start and 7.2 *N* at the end) an oily product, mp 95.5–96°, was isolated (in 54% crude yield), which is different from **2** and gives a positive ferric chloride test, suggesting that it is hydroxamide **6c** (R = H). The nature of this new product is currently under investigation.

(14) Based on the stereochemistry of **6a** deduced above, the ozonolysis product triacid (**19**) should be the *dl-erythro* stereoisomer. It is fortunate, from the viewpoint of the proof of structure, that the synthetic sample had the same stereochemistry as the ozonolysis product, since both *dl-erythro* and *dl-threo* stereoisomers are theoretically possible.

(15) The nmr spectra support the stereochemistry assigned to **12a** and its epimer **17**. In **12a** $J_{3,3a}$ = 10 Hz, consistent with the very small dihedral angle between the nearly eclipsed 3- and 3a-hydrogens, since the Karplus equation predicts a coupling constant of 10 Hz when the dihedral angle is zero.[16] In epimer **17**, $J_{3,3a}$ = 4 Hz, while the dihedral angle should be about 120°, which again is consistent with the prediction of a coupling constant of 4 Hz.[16]

(16) (a) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); (b) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 49–51.

(17) W. E. Parham, W. T. Hunter, and R. Hanson, *J. Amer. Chem. Soc.*, **73**, 5068 (1951).

coating the walls of the flask and the stirrer. At the end of the addition, the blue-green reaction mixture was allowed to come to room temperature and was stirred for 18 hr. At the end of this time the mixture had become light yellow and a brownish white precipitate was present, but there was none of the blue-green oil observed earlier. The precipitate was filtered and dried, giving a brown amorphous solid (43.6 g, 78%). This solid was dissolved in ethanol–benzene (1:1, 500 ml), producing a black solution, which was treated repeatedly with charcoal until the color became light yellow. The solution was concentrated to 250 ml and allowed to cool, causing separation of fluffy white needles (32.7 g, 43%), mp 198–201° dec. Four recrystallizations from ethanol–benzene gave fine white needles: mp 202–204° dec; $\lambda_{max}^{95\%\ EtOH}$ (a toluene chromophore[18]) mμ (log ε) 248 infl (2.18), 253 (2.24), 259 (2.30), 265 (2.18), 268 infl (1.86); ν_{max}^{Nujol} (cm^{-1}) 2640 (m, OH), 1667 (s, C=O), 1531 (mw); nmr (14% w/w in $(CH_3)_2SO$) τ 8.25 (m, 2.0, CH_2), 6.7 (m, 0.8, 3a-C**H**), 5.97 (d, 1.0, J = 11 Hz, 3-C**H**), 5.40 (bd, 1.0, J = 8 Hz, 6a-C**H**), 4.09 (m, 2.0, C**H**=C**H**), 2.73 (m, 5.0, C_6H_5), and 0.19 (s, O**H**). The compound was insoluble in sodium bicarbonate solution, but soluble in 5% sodium hydroxide solution and gave a bright purple color with ethanolic ferric chloride solution.

Anal. Calcd for $C_{13}H_{13}NO_2$ (215.24): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.31; H, 6.32; N, 6.37.

Methyl Derivative of 6a. 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-Hexahydro-1-methoxy-3-phenylcyclopenta[*b*]pyrrol-2-one (7).—A mixture of 1,-2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-phenylcyclopenta-[*b*]pyrrol-2-one (1.00 g, 4.65 mmol), potassium carbonate (0.55 g, 3.98 mmol), and methyl iodide (6.67 g, 47.0 mmol) in acetone (50 ml) was refluxed on a steam bath for 12 hr. Then more methyl iodide (6.67 g, 47.0 mmol) was added and refluxing was continued for 6 more hr. The acetone and excess methyl iodide were evaporated on a steam bath in a steam of air, leaving a yellow semisolid residue. The residue was extracted with hot water (25 ml). The resulting yellow oil was dissolved in methylene chloride and the aqueous layer was extracted with more methylene chloride. The methylene chloride solutions were combined, dried ($MgSO_4$), and evaporated, leaving a yellowish white solid (0.65 g, 61%), mp 107–111°. Two crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave long white needles: mp 113–114°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 248 infl (2.20), 253 (2.25), 259 (2.30), 265 (2.19), 268 infl (1.84); ν_{max}^{Nujol} (cm^{-1}) 1695 (s, C=O); nmr (22% w/w in $CHCl_3$-*d*) τ 8.00 (m, 2.2, CH_2), 6.74 (m, 1.4, 3a-C**H**), 6.12 (s, 3.3, OCH_3) superimposed on the upfield half of 6.04 (d, downfield half 0.4, J = 11 Hz, 3-C**H**), 5.33 (bd, 1.0, J = 8 Hz, 6a-C**H**), 4.08 (m, 2.0, C**H**=C**H**), and 2.76 (m, 4.7, C_6H_5). The compound was insoluble in 5% hydrochloric acid and 5% sodium hydroxide solution, and gave no color reaction with ethanolic ferric chloric solution.

Anal. Calcd for $C_{14}H_{15}NO_2$ (229.27): C, 73.34; H, 6.59; N, 6.11. Found: C, 73.18; H, 6.47; N, 5.98.

Acetyl Derivative of 6a. 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-Hexahydro-2-oxo-3-phenylcyclopenta[*b*]pyrrol-1-yl Acetate (8).—A solution of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (0.50 g, 2.32 mmol) and anhydrous sodium acetate (0.1 g) in acetic anhydride (15 ml, 159 mmol) was stirred at room temperature for 24 hr. The solution was poured into cold water (25 ml) and stirred to hydrolyze the excess acetic anhydride, causing an exothermic reaction. The warm solution was cooled in an ice bath, causing precipitation of a white solid (0.52 g, 87%), mp 115–117°. Three crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave white needles: mp 118–119°; ν_{max}^{Nujol} (cm^{-1}) 1785 and 1704 (s, C=O).

Anal. Calcd for $C_{15}H_{15}NO_3$ (257.28): C, 70.02; H, 5.88; N, 5.44. Found: C, 69.99; H, 5.61; N, 5.66.

Dihydro Derivative of 6a. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-1-hydroxy-3-phenylcyclopenta[b]pyrrol-2-one (9a).—A solution of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (0.50 g, 2.32 mmol) in methanol (100 ml) was hydrogenated at 2 atm over platinum oxide at room temperature for 36 hr. Filtration of the catalyst and evaporation of the pink solution left a reddish orange oil. The oil was dissolved in methylene chloride and precipitated with hot petroleum ether (bp 60–68°), giving a pink solid (0.45 g, 89%), mp 153–155°. Three recrystallizations from methylene chloride–petroleum ether gave fine white needles: mp 156.5–158°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 247 infl (2.18), 253 (2.23), 259 (2.29), 265 (2.17), 268 infl (1.88); ν_{max}^{Nujol} (cm^{-1}) 2680 (m, OH), 1668 (s, C=O), 1522 (m); nmr (12% w/w in $CHCl_3$-*d*) τ 8.50 (m, 5.2, 2.5 CH_2), 7.82 (m, 1.0, 0.5 CH_2), 6.99 (m, 0.9, 3a-C**H**), 5.87 (d, 1.2, J = 10 Hz, 3-C**H**) superimposed on part of 5.70 (m, 0.7, 6a-C**H**), and 2.67 (5.1, C_6H_5). The hydroxyl proton was not determined. The compound gave a bright purple color with ethanolic ferric chloride solution.

Anal. Calcd for $C_{13}H_{15}NO_2$ (217.26): C, 71.86; H, 6.96; N, 6.45. Found: C, 71.74; H, 7.05; N, 6.49.

Oxidation of **9a** with chromic acid in acetic acid gave benzoic acid (26%) as the only recognizable product.[1a] Attempted hydrolysis of **9a** in refluxing concentrated sulfuric acid for 24 hr (92% recovery) or in refluxing ethanolic aqueous sodium hydroxide for 4 hr (76% recovery) was unsuccessful, giving unchanged **9a**.[1a] The compound was also recovered unchanged (93%) after being heated in polyphosphoric acid solution at 115–120° for 15 min, and then poured into cold water.[1a] Attempted reduction of **9a** with lithium aluminum hydride in refluxing ether for 12 hr was also unsuccessful, giving unchanged **9a** in 87% recovery.[1a]

Acetyl Derivative of 8. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-2-oxo-3-phenylcyclopenta[*b*]pyrrol-1-yl Acetate (10). A. From Acetylation of 9a.—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (0.20 g, 0.92 mmol) and anhydrous sodium acetate (0.05 g) in acetic andydride (10 ml, 106 mmol) was stirred at room temperature for 5 hr. The solution was then poured into cold water (15 ml) and stirred. The warm solution resulting from exothermic hydrolysis of the acetic anhydride was cooled in an ice bath and scratched vigorously, causing separation of white needles (0.18 g, 75%), mp 108–110°. Several recrystallizations from methylene chloride–petroleum ether (bp 60–68°) gave fine white needles: mp 108–109°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 247 (2.17), 252 (2.24), 258 (2.31), 264 (2.17); ν_{max}^{Nujol} (cm^{-1}) 1785 and 1706 (s, C=O).

Anal. Calcd for $C_{15}H_{17}NO_3$ (259.29): C, 69.48; H, 6.61; N, 5.40. Found: C, 69.34; H, 6.76; N, 5.47.

B. From Hydrogenation of 8.—A solution of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-2-oxo-3-phenylcyclopenta[*b*]pyrrol-1-yl acetate (0.13 g, 0.51 mmol) in 95% ethanol (35 ml) was hydrogenated at 2 atm over platinum oxide at room temperature for 24 hr. Filtration of the catalyst and evaporation of the solvent left a light green solid (0.11 g, 82%), mp 100–103°. Two crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave white needles, mp 108–109°. There was no depression in mmp 108–109° with the sample prepared by acetylation of **9a**, and the infrared spectra in Nujol were identical.

Deoxo Derivative of 6a. 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-Hexahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (11).—1,2,3-*cis*-4,6a-*cis*-Hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (1.00 g, 4.65 mmol) was added to a mixture of iron filings (0.80 g, 14.3 mg-atom) in boiling glacial acetic acid (25 ml), and the resulting dark red mixture was refluxed for 48 hr. Most of the acetic acid was removed by distillation, water (200 ml) was added to the residue, and the mixture was cooled in an ice bath and basified with 2 *N* sodium hydroxide solution. The red, gelatinous iron (III) hydroxide was removed by gravity filtration and the light yellow filtrate was extracted exhaustively with methylene chloride. The extracts were dried ($MgSO_4$) and evaporated, leaving a yellowish white solid (0.75 g, 81%), mp 120–124°. Two crystallizations from ethanol–water gave white needles: mp 124.5–126°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 242 (2.00), 248 (2.06), 253 (2.19), 259 (2.30), 265 (2.18), 268 (1.98); ν_{max}^{Nujol} (cm^{-1}) 3330 (m, NH), 1689 and 1653 (s, C=O); nmr (21% w/w in $CHCl_3$-*d*) τ 7.56 (m, 2.0, CH_2), 6.99 (m, 1.1, 3a-C**H**), 6.65 (d, 1.0 , J = 7 Hz, 3-C**H**), 6.45 (bd, 0.9, J = 8 Hz, 6a-C**H**), 4.23 (m, 2.0, C**H**=C**H**), 2.70 (4.9, C_6H_5), and 1.60 (bs, N**H**). An ethanolic ferric chloride test was negative.

Anal. Calcd for $C_{13}H_{13}NO$ (199.24): C, 78.36; H, 6.58; N, 7.03. Found: C, 78.19; H, 6.50; N, 7.01.

Dihydrodeoxo Derivative of 6a. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (12a).—A solution of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (2.00 g, 9.28 mmol) in methanol (200 ml) was hydrogenated at 2 atm over Raney nickel at room temperature for 24 hr. Filtration of the catalyst and evaporation of the solvent left a white solid (1.85 g, 99%), mp 168–171°. Four crystallizations from methylene chloride–petroleum ether (bp

(18) Reported for toluene: $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 250 infl (1.98), 256 (2.15), 262 (2.28), 265 (2.10), 269 (2.19) [T. W. Campbell, S. Linden, S. Godshalk, and W. G. Young, *J. Amer. Chem. Soc.*, **69**, 880 (1947)]; $\lambda_{max}^{abs\ EtOH}$ mμ (log ε) 249 (2.11), 256 (2.27), 260 infl (2.33), 262 (2.40), 265 (2.24), 269 (2.33) [A. Fehnel and M. Carmack, *ibid.*, **71**, 84 (1949)].

60–68°) gave fine white needles: mp 171–172°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 243 (1.88), 248 (2.08), 253 (2.21), 259 (2.30), 265 (2.18), 268 infl (1.88); ν_{max}^{Nujol} (cm^{-1}) 3150 (mw, NH), 1684 (s, C=O); nmr (15% w/w in $CHCl_3$-*d*) τ 8.5 (m, 6.2, 3 CH_2), 7.0 (m, 0.9, 3a-CH), 5.92 (d, 1.9, J = 10 Hz, 3-CH) superimposed on 5.86 (m, 6a-CH), 2.65 (5.3, C_6H_5), and 2.11 (bs, 0.7, NH). That the 3 proton is coupled to the 3a proton was shown by a standard field sweep decoupling experiment with H_2 = 3 mG and a difference frequency of +64 Hz, which collapsed the doublet at 5.92.[19] The compound was soluble in concentrated hydrochloric acid but insoluble in aqueous sodium hydroxide. An ethanolic ferric chloride test was negative.

Anal. Calcd for $C_{13}H_{15}NO$ (201.26): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.72; H, 7.66; N, 7.11.

Similar hydrogenations with Raney nickel also gave the dihydrodeoxo derivative **12a** from the dihydro derivative **9a** (92%) in methanol, from the acetyldihydro derivative **10** (95%) in 95% ethanol, and with platinum oxide from the deoxo derivative **11** (46% yield after separation of some unchanged **11**), as shown by mixture melting point and infrared comparison in Nujol of the products with the sample prepared from hydrogenation of **6a**. Attempted oxidation of **12a** with chromium trioxide in glacial acetic acid at 0° gave unchanged **12a** in 100% recovery, but boiling with alkaline potassium permanganate solution gave benzoic acid (51%).[1a]

The lactam carbonyl group of **12a** was extremely resistant to hydrolysis and to reduction with lithium aluminum hydride, probably because of the steric hindrance of the adjacent phenyl substituent. Attempted hydrolysis gave unchanged **12a** from concentrated sulfuric acid at room temperature for 45 min (86% recovery) or from refluxing concentrated hydrochloric acid for 20 hr (96%).[1a] Attempted reduction with lithium aluminum hydride gave unchanged **12a** under the following conditions: (a) in ether for 24 hr (67% recovery), (b) with aluminum chloride in ether for 5 hr (70%), (c) in tetrahydrofuran for 24 hr (89%), and (d) in dioxane for 18 hr (38%).[1a]

Octahydrodeoxo Derivative of 12a. 3-Cyclohexyl-1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydrocyclopenta[*b*]pyrrol-2-one (13).—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (5.00 g, 24.9 mmol) in 95% ethanol (200 ml) was hydrogenated at 133 atm over Raney nickel (3 g) in an Aminco manganese-steel bomb. The temperature was raised gradually to 150° over a period of 2 hr (during which the pressure rose to 193 atm after 45 min), and heating was continued at this temperature for 2.5 more hr, with constant shaking. Cooling, filtration of the catalyst, evaporation of the solvent to one-third of its original volume, and addition of hot water (50 ml) caused precipitation of a white solid (4.90 g, 95%), mp 155–157°. Three crystallizations from ethanol–water gave white needles, mp 157.5–159°. The ultraviolet spectrum in 95% ethanol contained only rising end absorption; ν_{max}^{Nujol} (cm^{-1}) 3150 (ms, NH), 1678 (s, C=O).

Anal. Calcd for $C_{13}H_{21}NO$ (207.31): C, 75.31; H, 10.21; N, 6.76. Found: C, 75.39; H, 10.32; N, 6.70.

Attempted oxidation of **13** with chromic acid in acetic acid at room temperature for 1 hr was unsuccessful, giving unchanged **13** in 80% recovery.[1a]

N-Nitroso Derivative of 12a. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-1-nitroso-3-phenylcyclopenta[*b*]pyrrol-2-one (14).—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (1.00 g, 4.97 mmol) in concentrated hydrochloric acid (8 ml) was cooled to 0° in an ice bath. A solution of sodium nitrite (1.60 g, 23.3 mmol) in water (10 ml) was added dropwise with stirring, the temperature being maintained at 0°. The resulting yellow solid was filtered, washed repeatedly with water, and dried (0.95 g, 83%), mp 89–92°. Three crystallizations from 95% ethanol gave yellow needles: mp 92–94°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 251 (3.78), 430 (1.7), 451 (1.7); ν_{max}^{Nujol} cm^{-1} 1757 (s, C=O), 1497 (ms, N=O), 1347 (ms).

Anal. Calcd for $C_{13}H_{14}N_2O_2$ (230.20): C, 67.81; H, 6.13; N, 12.17. Found: C, 68.13; H, 6.02; N, 11.95.

The electronic spectrum of **14** is similar to that of 1-nitroso-2-pyrrolidinone [λ_{max} mμ (log ε) 252 (3.8), 423 (1.8)][20] and the N-nitroso derivative of **2** [$\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 261 (3.64), 402 (1.97), 418 (2.11), 439 (2.06)].[2a] Attempted nitrosation of **12a** in dilute, aqueous methanolic hydrochloric acid was unsuccessful.[1c] Solutions of **12a** (0.15 g, 0.75 mmol) in methanol (25 ml) and sodium nitrite (2.8 g, 41 mmol) in water (50 ml) were mixed, cooled to −2° in an ice–salt bath and added slowly to 3.3 *N* hydrochloric acid (13.8 ml) also at −2°, the temperature not being allowed to rise above 3°. Only unchanged **12a** was recovered, as a white solid, mp 170–171°. There was no depression in mmp 170–171°, with the starting material, and the infrared spectra in Nujol were identical.

Denitrosation of 14 to 12a.—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-1-nitroso-3-phenylcyclopenta[*b*]pyrrol-2-one (1.45 g, 6.29 mmol) in concentrated hydrochloric acid (25 ml) was refluxed for 24 hr. The solution was cooled and poured into cold water, causing precipitation of a yellowish white solid (1.05 g, 83%), mp 144–150°. Three crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave a sample, mp 171–172°. There was no depression in mmp 171–172° with the sample of **12a** prepared from hydrogenation of **6a** over Raney nickel, and the infrared spectra in Nujol were identical.

***p*-Nitro Derivative of 12a. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-(*p*-nitrophenyl)cyclopenta[*b*]pyrrol-2-one (15).**—A solution of sodium nitrate (0.40 g, 4.7 mmol) in concentrated sulfuric acid (20 ml) was added dropwise with stirring to a solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (1.00 g, 4.97 mmol) in concentrated sulfuric acid (30 ml) at 0° over a period of 0.5 hr. The resulting light yellow solution was stirred for 1 hr at 0° and then poured over chipped ice, causing precipitation of a light yellow solid (0.98 g, 80%), mp 135–150°. Three crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave pale yellowish white needles: mp 201–203°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 273 (4.03); ν_{max}^{Nujol} (cm^{-1}) 3140 (m, NH), 1694 (s, C=O), 1517 and 1350 (s, NO_2).

Anal. Calcd for $C_{13}H_{14}N_2O_3$ (246.26): C, 63.40; H, 5.73; N, 11.38. Found: C, 63.11; H, 5.80; N, 10.80, 11.53.

The ultraviolet spectrum is similar to that of *p*-nitrotoluene [$\lambda_{max}^{abs\ EtOH}$ mμ (log ε) 273 (3.98)].[21,22]

***p*-Amino Derivative of 12a. 3-(*p*-Aminophenyl)-1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydrocyclopenta[*b*]pyrrol-2-one (16).**—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-(*p*-nitrophenyl)cyclopenta[*b*]pyrrol-2-one (0.25 g, 1.01 mmol) in 95% ethanol (100 ml) was hydrogenated at 2 atm over platinum oxide at room temperature for 48 hr. Filtration of the catalyst and evaporation of the solvent left a cream-colored solid, which was dissolved in methylene chloride and filtered to remove a small amount of insoluble material. Hot petroleum ether (bp 60–68°) was added to the filtrate, causing precipitation of a pink solid (0.21 g, 96%), mp 185–203°, having an infrared spectrum in Nujol identical with that of the analytical sample. Six crystallizations from methylene chloride–petroleum ether gave cream-colored needles: mp 206–208°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 241 (4.02), 290 (2.9); ν_{max}^{Nujol} (cm^{-1}) 3360, 3300, 3160 (w, m, m, all NH), 1692 (s, C=O).

Anal. Calcd for $C_{13}H_{16}N_2O$ (216.27): C, 72.19; H, 7.46; N, 12.95. Found: C, 72.15; H, 7.27; N, 13.11.

Epimer of the Dihydrodeoxo Derivative. 1,2,3-*trans*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (17).

A. From Refluxing Ethanolic Aqueous Sodium Hydroxide.—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (0.50 g, 2.48 mmol) and sodium hydroxide (0.60 g, 15 mmol) in ethanol (30 ml) and water (20 ml) was refluxed for 6 hr. The resulting deep yellow solution was acidified with 10 *N* sulfuric acid (6 ml), causing the solution to become colorless. The ethanol was evaporated on a steam bath, and keeping and cooling the residual solution caused precipitation of a white solid (0.47 g, 94%), mp 120–123°. Three crystallizations from methylene chloride–petroleum ether (pb 60–68°) gave white needles: mp 124–125°; $\lambda_{max}^{95\%\ EtOH}$ mμ (log ε) 242 (2.00), 248 (2.09), 253 (2.22), 259 (2.31), 262 infl (2.20), 265 (2.19), 268 (2.02); ν_{max}^{Nujol} (cm^{-1}) 3300 (m, NH), 1690 and 1658 (s, C=O); nmr (11% w/w in $CHCl_3$-*d*) τ 8.32 (6.1, 3 CH_2), 7.17 (bm, 1.1, 3a-CH), 6.68 (d, 1.0, J = 4 Hz, 3-CH), 5.83 (m, 1.1, 6a-CH), 2.69 (5.0, C_6H_5), and 2.31 (b, 0.7, NH).

Anal. Calcd for $C_{13}H_{15}NO$ (201.26): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.48; H, 7.51; N, 7.22.

(19) We are indebted to Richard F. Sprecher for carrying out this experiment.

(20) R. Huisgen and J. Reinertshofer, *Ann. Chem.*, **575**, 197 (1952).

(21) W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, *Anal. Chem.*, **23**, 1740 (1951). This reference reports for *o*-nitrotoluene: $\lambda_{max}^{abs\ EtOH}$ mμ (log ε) 257 (3.73).

(22) For *m*-nitrotoluene: $\lambda_{max}^{abs\ EtOH}$ mμ (log ε) 264 (3.83); G. N. Jean and F. F. Nord, *J. Org. Chem.*, **20**, 1370 (1955).

Epimerization of **12a** was also observed (a) during attempted Hofmann rearrangement in methanolic aqueous sodium hydroxide containing bromine (67% yield of **17**), (b) during attempted reduction with lithium aluminum hydride for 7 days in refluxing ether (53%), (c) in refluxing hydrazine for 12 hr (84%), and (d) in refluxing hydrobromic acid in acetic acid for 4 days (90%).

B. From Refluxing Ethanolic Aqueous Potassium Hydroxide. Isolation of a Dimorphic Form.—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (0.75 g, 3.73 mmol) and potassium hydroxide (1.00 g, 17.8 mmol) in ethanol (30 ml) and water (20 ml) was refluxed for 3 hr. The solution was cooled to room temperature and neutralized by dropwise addition of concentrated sulfuric acid, causing precipitation of a white solid (K_2SO_4; soluble in water, insoluble in methylene chloride, leaves a residue upon ignition). The solid was filtered, and the filtrate was diluted with water and extracted repeatedly with methylene chloride. The extracts were dried ($MgSO_4$), evaporated almost to dryness, and diluted with petroleum ether (bp 60–68°), causing separation of a white precipitate (0.67 g, 89%), mp 120–124°. Three crystallizations from methylene chloride–petroleum ether gave white needles, mp 126.5–128.5°, having an infrared spectrum in Nujol different from that of the samples described in part A, not only in the "fingerprint region" but also in the facts that there is a single band in the carbonyl region while the NH absorption is split: ν_{max}^{Nujol} (cm^{-1}) 3160 and 3050 (m, NH), 1695 (s, C=O).

Dibenzyl Derivative of the Dihydrodeoxo Derivative or of Its Epimer. 1,3-*cis*(?)-Dibenzyl-1,2,3,3a-*cis*-4,5,6,6a-*cis*-octahydro-3-*trans*(?)-phenylcyclopenta[*b*]pyrrol-2-one (18). A. From the Dihydrodeoxo Derivative.—Sodium hydride dispersed in oil (2.1 g, containing 0.96 g, 40 mmol of NaH) was added to a solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (4.00 g, 19.9 mmol) in N,N-dimethylformamide (75 ml), and the mixture was stirred for 15 min. Benzyl chloride (2.53 g, 20.0 mmol) was added and the mixture was refluxed for 3 hr. Additional benzyl chloride (2.53 g, 20.0 mmol) was added and refluxing was continued for 12 more hr. The bulk of the N,N-dimethylformamide was removed by distillation at reduced pressure, leaving a dark brown, viscous oil. Water (25 ml) and methylene chloride (75 ml) were added, and the methylene chloride layer was separated, dried ($MgSO_4$), and concentrated. The resulting dark brown oil was dissolved in a minimum of benzene and chromatographed on alumina which had been packed wet with petroleum ether (bp 60–68°). Elution with petroleum ether and mixtures with benzene removed nothing, but elution with benzene removed a yellowish white solid (1.56 g, 21%), mp 101–102.5°. Three crystallizations from ethanol–water gave fine white needles: mp 102–103°; ν_{max}^{Nujol} (cm^{-1}) 1679 (s, C=O).

Anal. Calcd for $C_{27}H_{27}NO$ (381.49): C, 85.00; H, 7.13; N, 3.67. Found: C, 84.68; H, 7.27; N, 3.83.

Attempted reduction with lithium aluminum hydride in refluxing ether for 8 hr was unsuccessful, giving unchanged **18** in 90% recovery.[1a]

B. From the Epimer of the Dihydrodeoxo Derivative. 1,2,3-*trans*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (1.00 g, 4.97 mmol) was added to a mixture of sodium hydride dispersed in oil (0.50 g, containing 0.24 g, 10 mmol of NaH) and N,N-dimethylformamide (25 ml), and the mixture was stirred for 15 min. Benzylation with two portions of benzyl chloride (0.63 g, 4.98 mmol each) separated by 3 hr of refluxing, followed by an additional 24 hr of refluxing and work-up in the general manner described for benzylation of the dihydrodeoxo derivative (part A above), gave from chromatography a yellowish white solid (0.53 g, 28%), mp 98–101°. Three crystallizations from ethanol–water gave white needles, mp 102–103°. There was no depression in mmp 102–103° with the sample prepared from the dihydrodeoxo derivative, and the infrared spectra in Nujol were identical.

Independent Synthesis of the Epimer of the Dihydrodeoxo Derivative. A. Ethyl 2-Oxo-α-phenylcyclopentaneacetate (26).—The general method is that of Stork and coworkers.[23] Ethyl α-bromophenylacetate[24] (99.5 g, 410 mmol; $n^{26}D$ 1.5336; ν_{max}^{neat} (cm^{-1}) 1740 (s, C=O)) was added dropwise to a solution of freshly prepared 1-(1-cyclopenten-1-yl)pyrrolidine (50.0 g, 364 mmol; obtained[23,25] in 99% yield, bp 85–89° (14 mm), $n^{25}D$ 1.5126) in dry methanol (300 ml) and the solution was refluxed for 18 hr. Water (15 ml) was added and the solution was refluxed for 1 additional hr. The cooled solution was diluted with water (800 ml) and extracted with methylene chloride, and the extracts were dried ($MgSO_4$) and evaporated, leaving a red oil. Fractional distillation at reduced pressure gave a light yellow oil (38.7 g, 43%): bp 148–152° (0.3–0.4 mm); $n^{24}D$ 1.5188; ν_{max}^{neat} (cm^{-1}) 3420 (w, C=O overtone), 1724 (s, broad, C=O).

2,4-Dinitrophenylhydrazone of 26.—A solution of ethyl 2-oxo-α-phenylcyclopentaneacetate (0.50 g, 2.03 mmol) in 95% ethanol (10 ml) was added to a warm solution of 2,4-dinitrophenylhydrazine (0.41 g, 2.07 mmol) and concentrated sulfuric acid (2 ml) in water (3 ml) and 95% ethanol (10 ml), and the solution was allowed to cool to room temperature, producing a light yellow precipitate (0.79 g, 91%), mp 196–198°. Four crystallizations from methanol–chloroform gave fine yellow needles: mp 198–200°; ν_{max}^{Nujol} (cm^{-1}) 3300 (w, NH), 1726 (s, C=O), 1520, 1344, 1314 (s, NO_2).

Anal. Calcd for $C_{21}H_{22}N_4O_6$ (426.24): C, 59.15; H, 5.20; N, 13.14. Found: C, 59.10; H, 5.18; N, 13.24.

B. Saponification of 26 to the Acid. 2-Oxo-α-phenylcyclopentaneacetic Acid (27).—A solution of ethyl 2-oxo-α-phenylcyclopentaneacetate (10.0 g, 40.6 mmol) and aqueous 10% potassium hydroxide (91.2 g, 164 mmol) in the minimum amount of ethanol was refluxed for 24 hr. The solution was cooled, acidified with dilute sulfuric acid, and extracted with ether. The ether extract was extracted exhaustively with saturated sodium bicarbonate solution, and the bicarbonate extracts were acidified with dilute sulfuric acid and extracted with ether. Evaporation of the ether left a yellow oil, which crystallized after being kept for a time, giving a sample (6.36 g), mp 142–145°. Evaporation of the original reaction solution gave another crop of yellowish white crystals (1.85 g), mp 141–145°. The combined crops (8.21 g, 92%) were recrystallized to constant melting point from acetone–water, giving white needles: mp 143.5–145°; ν_{max}^{Nujol} (cm^{-1}) 2700 (mw, broad, OH), 1738 and 1701 (s, C=O).

Anal. Calcd for $C_{13}H_{14}O_3$ (218.24): C, 71.54; H, 6.47. Found: C, 71.52; H, 6.63.

C. Reductive Amination and Lactamization of 27 to the Epimer of the Dihydrodeoxo Derivative. 1,2,3-*trans*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-phenylcyclopenta[*b*]pyrrol-2-one (17).—The compound was prepared according to the general method of Bertho and Rödl[26] for the model compound, octahydrocyclopenta[*b*]pyrrol-2-one. A solution of 2-oxo-α-phenylcyclopentaneacetic acid (2.00 g, 9.15 mmol) in concentrated ammonium hydroxide (15 ml) was saturated at −10° with liquid ammonia. The cold solution was placed in a manganese–steel bomb and cooled to Dry Ice–acetone temperature. Raney nickel (0.5 g) was added and the bomb was sealed, charged with hydrogen at 133 atm, and heated gradually to 100° with constant shaking. The bomb was then heated quickly to 150° and kept at this temperature for 2 hr. Then the bomb was allowed to cool, opened, and the catalyst removed by filtration. The dark brown filtrate was evaporated in a rotary evaporator, leaving a brown solid, which was washed with water, filtered, and dried (0.35 g, 19%), mp 112–123°. Three crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave white needles (11%), mp 128.5–129.5°. There was no significant depression in mmp 125.5–128.5°, with the dimorphic form (mp 126.5–128.5°) of the epimer of the dihydrodeoxo derivative (part B), and the infrared spectra in Nujol were identical. The nmr spectrum of a 10% by weight solution in $CHCl_3$-*d* was identical with that of the original dimorph of the epimer (part A), and the ultraviolet spectra in 95% ethanol were also essentially identical.

Anal. Calcd for $C_{13}H_{15}NO$ (201.26): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.33; H, 7.50; N, 7.02.

Ozonolysis of 6a. 1-Phenylpropane-1,2,3-tricarboxylic Acid (19). A. Followed by Performic Acid Oxidation at Room Temperature.—A stream of ozonized oxygen from a Welsbach T-23 ozonizer was bubbled through a well-stirred suspension of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (4.00 g, 18.6 mmol) in methanol (200 ml) at −78° until all the solid had disappeared and the solid had become dark blue. The resulting cold solution was then flushed with oxygen for 0.5 hr and allowed to come to room temperature.

(23) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(24) (a) R. Anschütz, C. Hahn, and P. Walter, *Ann. Chem.*, **354**, 127 (1907); (b) C. S. Marvel, E. J. Prill, and D. F. DeTar, *J. Amer. Chem. Soc.*, **69**, 52 (1947).

(25) M. E. Kuehne, *ibid.*, **81**, 5400 (1959).

(26) A. Bertho and G. Rödl, *Chem. Ber.*, **92**, 2218 (1959).

The methanol was carefully removed at room temperature in a rotary evaporator under high vacuum, leaving a light yellow, viscous oil. The oil was dissolved in 90% formic acid (25 ml), and 30% hydrogen peroxide (8.00 g, 70.5 mmol) in 90% formic acid (15 ml) was added dropwise with vigorous stirring. The resulting yellow solution was stirred at room temperature for 24 hr. The formic acid was carefully removed at room temperature in a rotary evaporator under high vacuum, leaving a viscous brown oil. The oil was dissolved in saturated sodium bicarbonate solution (75 ml), washed with ether, and acidified with concentrated hydrochloric acid. The acidified solution was extracted with ether in a continuous liquid–liquid extractor for 24 hr. The ether extract was dried ($MgSO_4$) and evaporated, leaving a light yellow glassy oil, which crystallized on scratching to a light yellow solid (2.58 g, 55%), mp 175–185°. Three recrystallizations from acetone–acetonitrile and one from water gave fine white needles, mp 202–203°. The infrared spectrum in Nujol was identical with that of the sample isolated by performic acid oxidation under exothermic conditions. There was no depression in mmp 202–204° with the synthetic sample, and the infrared spectra in Nujol were identical.

B. Followed by Performic Acid Oxidation under Exothermic Conditions.—1,2,3-*cis*-3a-*cis*-4,6a-*cis*-Hexahydro-1-hydroxy-3-phenylcyclopenta[*b*]pyrrol-2-one (6.00 g, 27.9 mmol) in methanol (300 ml) was ozonized in the manner described in part A, giving, after evaporation of the methanol, a light pink, viscous oil. The oil was dissolved in 90% formic acid (25 ml), and 30% hydrogen peroxide (12.0 g, 106 mmol) in 90% formic acid (15 ml) was added dropwise with vigorous stirring. The resulting yellow solution was heated gradually to 53°, at which point the reaction became quite exothermic, and the temperature rose rapidly to 110°. After the initial reaction had subsided, the solution was refluxed for 1 hr, during which it became quite dark. The formic acid was removed in a rotary evaporator, leaving a viscous brown tar. The tar was extracted with saturated sodium bicarbonate solution (75 ml), causing most of the tar to dissolve but leaving behind a dark brown gum. The bicarbonate solution was washed with benzene and chloroform, acidified with concentrated hydrochloric acid, and extracted as described in part A, giving a tan solid (1.66 g, 24%), mp 170–190°, having an infrared spectrum in Nujol identical with that of the analytical sample. Four crystallizations from acetone–acetonitrile and one from acetone–water gave fine white needles: mp 203–205°; ν_{max}^{Nujol} (cm^{-1}) 3070 (ms) and 2640 (m, OH), 1704 (s) and 1670 (ms, C=O).

Anal. Calcd for $C_{12}H_{12}O_6$ (252.22): C, 57.14; H, 4.80. Found: neutralization equivalent, 88.5; C, 57.14; H, 4.88.

The infrared spectrum in Nujol was identical with that of the sample isolated by performic acid oxidation at room temperature. There was no depression in mmp, 203–205°, with the synthetic sample, and the infrared spectra in Nujol were identical.

Synthesis of the Ozonolysis Product. 1-Phenylpropane-1,2,3-tricarboxylic Acid (19). A. Mandelonitrile.—The compound was obtained[27] in 84% yield as a yellow oil: ν_{max}^{neat} (cm^{-1}) 3410 (s, OH), 2250 and 2210 (w, C≡N), 1701 (s, C=O, probably from unreacted benzaldehyde).

B. Diethyl 2,3-Dicyano-3-phenylpropane-1,2-dicarboxylate.—The compound was prepared[4] by sodium ethoxide catalyzed condensation of benzaldehyde (liberated *in situ* from mandelonitrile) with ethyl cyanoacetate, followed by nucleophilic addition of cyanide ion (also derived from the mandelonitrile) and nucleophilic attack of the resulting anion on ethyl chloroacetate. Through an apparent omission in print, the original reference[4] fails to mention that the product, after dilution with water, was worked up by extraction with ether. In the present work, the extract was subsequently dried ($MgSO_4$), the ether evaporated, and the viscous orange residue distilled, giving the product in 35% yield as a viscous, glassy syrup: bp 165–175° (0.2–0.35 mm); ν_{max}^{neat} (cm^{-1}) 3470 (mw, C=O, probably an overtone), 3370 (w, OH, possibly from the ethanol solvent), 2240 (m, C≡N), 1740 (vs, broad, C=O) [lit.[4] yield 39%, bp 205–207° (4 mm)].

C. 1-Phenylpropane-1,2,3-tricarboxylic Acid (19).—The compound was prepared from the diethyl dicyano ester by hydrolysis first in boiling aqueous (1:1 by volume) sulfuric acid and then in 15% sodium hydroxide solution according to the procedure of Chatterjee and Barpujari.[4] It was obtained as a light red oil which crystallized on cooling and scratching, giving a light yellow solid in 76% yield, mp 184–188°, having an infrared spectrum in Nujol identical with that of the purified sample. Two recrystallizations from acetone–acetonitrile and two from water gave fine white needles, mp 204–206° [lit. (no yield stated[4]) mp 199°,[28] 204°[4]]; monohydrate mp (rapid heating) 110°, decomposes strongly at 125.[29]

Rearrangement of the Sodium Salt of 6-Methyl-5-nitro-2-norbornene in Aqueous Methanolic Hydrochloric Acid. 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-Hexahydro-1-hydroxy-3-methylcyclopenta[*b*]pyrrol-2-one (6b).—A solution of 6-methyl-5-nitro-2-norbornene[30] (12.0 g, 78.3 mmol) and aqueous 20% sodium hydroxide (31.2 g, 155 mmol of NaOH) in methanol (20 ml) was kept overnight in a freezer (at about −15°). The cold solution was then added dropwise with vigorous stirring over 0.5 hr to concentrated hydrochloric acid (75 ml, 900 mmol) cooled to −5° in an ice–salt bath. The yellow solution was allowed to come to room temperature and was stirred for 24 hr. The now dark red solution was diluted to twice its volume with cold water and was extracted exhaustively with methylene chloride. The extracts were dried ($MgSO_4$) and evaporated, leaving a dark red oil. The oil was continuously triturated with small amounts of hot petroleum ether (bp 90–100°) until the extracts were no longer colored, leaving a black, foul smelling, tarry residue. The extracts were concentrated on a rotary evaporator, leaving a light yellow oil (5.30 g) which, upon being kept for a time, partially crystallized to a yellow waxy solid. Trituration with a very small amount of cold (0°) ether gave a white solid (4.78 g, 40%), mp 80–85°. Four crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave fluffy white needles: mp 88–89.5°; ν_{max}^{Nujol} (cm^{-1}) broad OH band obscured by CH bands, 1686 and 1664 (s, C=O), 1524 (m); nmr (21% w/w in $CHCl_3$-*d*) τ 8.87 (d, 3.0, J = 7 Hz, $CHCH_3$), 7.62 and 7.51 (2.1, CH_2), 7.42–6.82 (m, 1.9, 3a-CH and 3-CH), 5.35 (finely split d, 1.1, J = 7 Hz, 6a-CH), and 3.98 (s, 1.9, CH=CH). The hydroxyl proton was not determined. The compound gave a bright purple color with ethanolic ferric chloride.

Anal. Calcd for $C_8H_{11}NO_2$ (153.18): C, 62.72; H, 7.24; N, 9.14. Found: C, 62.37; H, 7.34; N, 8.93.

Ozonolysis of **6b** and work-up in the manner described for the phenyl derivative gave an acidic, reddish black oil (16 wt %). An attempt to characterize the oil by formation of an amide by treatment with thionyl chloride and then ammonia gave no solid product.

Dihydro Derivative of 6b. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-1-hydroxy-3-methylcyclopenta[*b*]pyrrol-2-one (9b).—A solution of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-methylcyclopenta[*b*]pyrrol-2-one (0.15 g, 0.98 mmol) in 95% ethanol (50 ml) was hydrogenated at 2 atm over platinum oxide at room temperature for 6 hr. Filtration of the catalyst and evaporation of the solvent left a clear oil, which upon cooling and scratching crystallized to a white solid (0.14 g, 92%), mp 101–105°. Four recrystallizations from methylene chloride–petroleum ether (bp 60–68°) gave fine white needles: mp 106–107°; ν_{max}^{Nujol} (cm^{-1}) broad OH band obscured by CH bands, 1687 and 1653 (s, C=O), 1530 (m); nmr (12% w/w in $CHCl_3$-*d*) τ 8.89 (d, 3.2, J = 7 Hz, $CHCH_3$), 8.40 (m, 5.0, 2.5 CH_2), 7.84 (m, 0.8, 0.5 CH_2), 7.3 (m, 2.0, 3a-CH and 3-CH), and 5.80 (b, 1.0, 6a-CH). The hydroxyl proton was not determined. The compound gave a bright purple color with ethanolic ferric chloride solution.

Anal. Calcd for $C_8H_{13}NO_2$ (155.19): C, 61.91; H, 8.44; N, 9.03. Found: C, 61.76; H, 8.48; N, 9.23.

Dihydrodeoxo Derivative of 6b. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-methylcyclopenta[*b*]pyrrol-2-one (12b). A. From Hydrogenation of 6b.—A solution of 1,2,3-*cis*-3a-*cis*-4,6a-*cis*-hexahydro-1-hydroxy-3-methylcyclopenta[*b*]pyrrol-2-one (0.50 g, 3.26 mmol) in 95% ethanol (50 ml) was hydrogenated at 2 atm over Raney nickel at room temperature for 20 hr. Filtration of the catalyst and evaporation of the solvent left a white solid (0.44 g, 97%), mp 80–85°. Three crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave white plates: mp 85–86°, which gave a depression in mmp 48–55°, with the starting material; ν_{max}^{Nujol} (cm^{-1}) 3170 (ms, NH), 1678–1655 (s, broad, C=O); nmr (12% w/w in $CHCl_3$-*d*) τ 8.85 (d, 3.4, J = 7 Hz, $CHCH_3$), 8.32 (6.1, 3 CH_2), 7.3 (m, 1.9, 3a-CH and 3-CH), 5.91 (m, 0.9,

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6a-CH), and 2.53 (b, 0.7, NH). An ethanolic ferric chloride test was negative.

Anal. Calcd for $C_8H_{13}NO$ (139.19): C, 69.03; H, 9.41; N, 10.06. Found: C, 69.25; H, 9.41; N, 9.98.

Compound **12b** did not epimerize, being recovered unchanged in 67% yield from refluxing ethanolic aqueous sodium hydroxide for 6 hr under conditions which caused the phenyl dihydrodeoxo derivative (**12a**) to epimerize to **17**.[1a]

B. From Hydrogenation of 9b.—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-1-hydroxy-3-methylcyclopenta[*b*]pyrrol-2-one (0.10 g, 0.64 mmol) in 95% ethanol (20 ml) was hydrogenated at 2 atm over Raney nickel at room temperature for 24 hr. Filtration of the catalyst and evaporation of the solvent left a white solid (0.075 g, 84%), mp 76–82°. Three crystallizations from methylene chloride–petroleum ether (bp 60–68°) gave colorless plates, mp 85–86°. There was no depression in mmp 85–86° with the sample prepared from hydrogenation of **6b** (part A above), and the infrared spectra in Nujol were identical.

Monobenzyl Derivative of the Dihydrodeoxo Derivative. 1-Benzyl-1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-methylcyclopenta[*b*]pyrrol-2-one (28).—Sodium hydride dispersed in oil (0.74 g, containing 0.35 g, 14.6 mmol of NaH) was added to a solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-methylcyclopenta[*b*]pyrrol-2-one (1.00 g, 7.18 mmol) in N,N-dimethylformamide (25 ml), and the mixture was stirred for 15 min. Benzyl chloride (0.91 g, 7.19 mmol) was added and the mixture was refluxed for 3 hr. Additional benzyl chloride (0.91 g, 7.19 mmol) was added and refluxing was continued for 24 more hr. Work-up and chromatography in the manner described for preparation of the dibenzyl derivative **18** gave a light yellow liquid (0.87 g, 53%). Distillation under high vacuum gave a colorless liquid: bp 80–100° (0.001 mm); $n^{30}D$ 1.5388; ν_{max}^{neat} (cm^{-1}) 3400 (mw, C=O overtone(?), 1669 (s, C=O).

Anal. Calcd for $C_{15}H_{19}NO$ (229.31): C, 78.56; H, 8.35; N, 6.11. Found: C, 78.62; H, 8.34; N, 6.13.

Hydrolysis of the Dihydrodeoxo Derivative with Concentrated Hydrochloric Acid. 2-*cis*-Amino-α-methylcyclopentaneacetic Acid Hydrochloride (29).—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-methylcyclopenta[*b*]pyrrol-2-one (0.30 g, 2.16 mmol) in concentrated hydrochloric acid (20 ml) was refluxed for 16 hr. The solvent was removed in a rotary evaporator, leaving white needles (0.28 g, 68%), mp 184–191°. Three recrystallizations from absolute ethanol–ether gave white needles: mp 189.5–191°; ν_{max}^{Nujol} (cm^{-1}) 2570 (m), 2450 (mw), 2020 (mw), 1990 (mw), 1890 (w), 1621 (s), 1572 (m), 1532 (s), all NH_3^+, and 1720 (s, C=O).

Anal. Calcd for $C_8H_{16}NO_2Cl$ (193.67): C, 49.61; H, 8.33; N, 7.23. Found: C, 49.18; H, 8.42; N, 7.33.

Reduction of the Dihydrodeoxo Derivative with Lithium Aluminum Hydride. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-methylcyclopenta[*b*]pyrrole (30).—A solution of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-methylcyclopenta[*b*]pyrrol-2-one (1.00 g, 7.19 mmol) in dry ether (25 ml) was added dropwise under nitrogen at a rate to maintain a steady reflux to a suspension of lithium aluminum hydride (0.62 g, 16.3 mmol) in dry ether (25 ml). The mixture was then refluxed for 20 hr, stirred at room temperature for 2 hr, cooled in an ice bath, and the excess lithium aluminum hydride was destroyed by cautious addition of cold water. The ether layer was decanted and the solid residue was extracted twice with warm ether. The extracts were combined with the ether decantate, and the ether was removed in a rotary evaporator at room temperature, leaving a yellow oil. The oil was dissolved in 5.6% hydrochloric acid (25 ml), washed with ether, basified with aqueous 5% sodium hydroxide, and extracted exhaustively with ether. The ether extracts were dried (KOH) and evaporated in a rotary evaporator at room temperature, leaving a colorless oil (0.85 g, 94%): $n^{24}D$ 1.4776; ν_{max}^{neat} (cm^{-1}) 3240 (s, NH), 1695 (m, NH).

***p*-Toluenesulfonyl Derivative of 30. 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-Octahydro-3-methyl-1-(*p*-toluenesulfonyl)cyclopenta[*b*]pyrrole.**—*p*-Toluenesulfonyl chloride (0.16 g, 0.84 mmol) was added to a suspension of 1,2,3-*cis*-3a-*cis*-4,5,6,6a-*cis*-octahydro-3-methylcyclopenta[*b*]pyrrole (0.10 g, 0.80 mmol) in aqueous 5% sodium hydroxide (5 ml, 6.2 mmol). The mixture was stirred at room temperature for 8 hr, giving a precipitate (0.21 g, 94%), mp 106–109°. Two crystallizations from ethanol–water gave white plates: mp 110–111°; ν_{max}^{Nujol} (cm^{-1}) no NH, 1338 and 1160 (s, C=O).

Anal. Calcd for $C_{15}H_{21}NO_2S$ (279.39): C, 64.48; H, 7.58; N, 5.01; S, 11.48. Found: C, 64.11; H, 7.59; N, 4.83; S, 11.79.

Registry No.—**6a,** 19759-07-0; **6b,** 19759-08-1; **7,** 19759-09-2; **8,** 19759-10-5; **9a,** 19759-11-6; **9b,** 19759-12-7; **10,** 19759-13-8; **11,** 19759-14-9; **12a,** 19759-15-0; **12b,** 19759-16-1; **13,** 19765-72-1; **14,** 19765-73-2; **15,** 19765-74-3; **16,** 19765-75-4; **17,** 19765-76-5; **18,** 19765-77-6; **19,** 19765-78-7; **26** (2,4-dinitrophenylhydrazone), 19755-90-9; **27,** 19775-91-0; **28,** 19759-17-2; **29,** 19759-18-3; **30** (*p*-toluenesulfonyl deriv), 19759-19-4.

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