carbon monoxide, 10 ml. of 0.3*M* dicobalt octacarbonyl in hexane was syringed into the flask followed by 3 ml. of dimethylformamide. After the evolution of carbon monoxide ceased (30 min.), the mixture was cooled to 0° and 6 ml. of 12*N* hydrochloric acid added dropwise with (magnetic) stirring. The lower layer was syringed off and the remaining 0.4*M* cobalt hydrocarbonyl in hexane washed with 10 ml. of oxygen-free water. In the experiments where a nitrogen atmosphere was desired, the system was purged with nitrogen at this point. If, anhydrous cobalt hydrocarbonyl was desired, the solution was cooled to −70° and the hexane solution syringed off the ice and transferred to another flask under carbon monoxide or nitrogen as desired.

Hydroformylation. To the 0.4*M* solution of cobalt hydrocarbonyl, prepared as described above, the desired quantity of pentene was added and the solution stirred for the desired time. In the experiments in which the total volume was of interest (Table II) the pentene was diluted with the appropriate volume of hexane; otherwise the total volume was 10 ml. plus the volume of added pentene. At the end of the reaction time, 3 ml. dimethylformamide or 2 ml. of quinoline was added, and the mixture stirred until evolution of carbon monoxide stopped. Two milliliters of reaction mixture was then slowly distilled under vacuum with stirring into a test tube at −70° and the material collected was used for vapor phase chromatography analysis for olefins. To the residue, 20 ml. of water was added, and after stirring the mixture for 5 min., the hydrocarbon layer was sampled for aldehyde analysis by vapor phase chromatography. The data are summarized in the tables in the text.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Structure of Pernitroso Compounds of *t*-Alkyl Ketones[1]

JEREMIAH P. FREEMAN

Received April 17, 1961

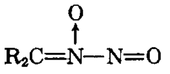
The nitrimine structure, $R_2C{=}N{-}NO_2$, previously proposed for the so-called pernitroso compounds derived from *t*-alkyl ketoximes, is supported by infrared and ultraviolet spectral evidence and by the conversion of these compounds to primary nitramines with complex hydrides.

The reaction of ketoximes with nitrosating agents to regenerate the parent ketone has been used extensively as a synthetic tool but the course of the reaction and the nature of the intermediates are only partly understood.[2,3] In a few instances, pseudonitroles are produced.[4] In most cases the intermediates are not isolated but decompose under the conditions of the reaction to ketone and nitrous oxide.[5] However, certain terpenoid and steroid ketoximes yield pernitroso compounds[6] which can be isolated and which in turn are convertible to the parent ketones by hydrolysis.[6a] The distinguishing characteristic of pernitroso compounds prepared by this reaction is the presence of a tertiary alkyl group attached to the oximino group; the stability of these compounds apparently depends upon this group.[7,10]

A number of structural formulas have been suggested for these compounds. The Italian school originally proposed the oxime nitrite structure (I) which was subsequently abandoned in favor of the *N*-nitrosooxime formulation (II).[11] This latter formulation was favored by Fusco and his co-

$R_2C{=}N{-}ONO$

I

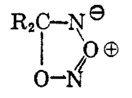


$R_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}N{=}O$

II

$R_2C{=}N{-}NO_2$

III



IV

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[1] This research was carried out under Army Ordnance Contract DA-01-021-ORD-11878.

[2] D. T. Manning and H. A. Stansbury, Jr., *J. Am. Chem. Soc.*, **81**, 4885 (1959). This article contains a good bibliography of this reaction.

[3] (a) Aldoximes undergo more complicated reactions including oxidation and nitration [J. H. Boyer and H. Alul, *J. Am. Chem. Soc.*, **81**, 4237 (1959)]. (b) Recently it has been shown that azine bisoxides are common oxidation products of aromatic aldoximes [L. Horner, L. Hockenberger, and W. Kirmse, *Chem. Ber.*, **94**, 290 (1961)].

[4] R. Scholl, *Ber.*, **18**, 507 (1885).

[5] A few steroid ketoximes yield nitrogen rather than nitrous oxide.

[6] Pernitroscocamphor was obtained along with camphor from the reaction of the sodium salt of camphor oxime and perchloryl fluoride. The appearance of this material confirms the suggestion that nitrosating agents are produced during this reaction [J. P. Freeman, *J. Am. Chem. Soc.*, **82**, 3869 (1960)].

[6a] For example, see A. Gandini, *Gazz. chim. ital.*, **72**, 232 (1942).

[7] The only known exception to this rule is that of pernitrosomesityl oxide.[8] Its structure has been shown[9] to be different from that of the pernitroso compounds discussed in this article.

[8] C. Harries and R. Gley, *Ber.*, **32**, 1330 (1899).

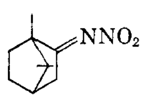
[9] J. P. Freeman, to be published.

[10] A number of new compounds containing the pernitroso group have been prepared by the action of nitric oxide on azine bisoxides.[3b] The nitrimine structure (III) was assigned on the basis of spectral and chemical properties. Under the nonhydrolytic conditions of this reaction, these nitrimines, which do not possess *t*-alkyl groups, survive.

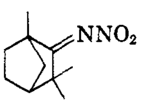
[11] O. Angelucci, *Ann.*, **341**, 172 (1905).

workers[12] for pernitrosomesityl oxide; this was subsequently proved to be incorrect.[9] By inference, all pernitroso compounds were believed to have the same structure.[12] Scholl[13] favored the nitrimine structure (III) based upon his investigations of pernitrosopinacolone. This nitrimine structure was favored by Wright[14] because of the similarity in chemical behavior of pernitrosocamphor and furfuralnitrimine. The latter compound was prepared from furfural and nitramide. Recently, the mesoionic structure (IV) was suggested.[15]

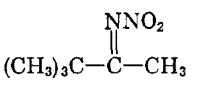
Spectral properties. Preliminary evidence was reported recently to support the nitrimine structure (V) for pernitrosocamphor.[16] Additional evidence is presented here to support this type of structure for the terpene pernitroso compounds and for pernitrosopinacolone. Three compounds were examined: pernitrosocamphor (V), pernitrosofenchone (VI), and pernitrosopinacolone (VII). The infrared spectra of each of the compounds contains strong bands[17] at 1560–1570 and 1310–1320 cm.$^{-1}$, and medium bands at 1620–1640 cm.$^{-1}$ The two strong bands may be assigned to the asymmetric and symmetric stretching vibrations of the nitro group,[18] and the medium band to the imine, C=N, stretching frequency[19] of a nitrimine structure (III).[20]



V



VI



$(CH_3)_3C-\overset{\overset{NNO_2}{\|}}{C}-CH_3$

VII

The oxime nitrite structure (I) cannot be accommodated by these spectra as nitrites exhibit a characteristic doublet[21] in the region of 1650 and 1620 cm.$^{-1}$ The spectral characteristics of structures II and IV are only speculative, but it is difficult to assign these three bands to specific vibrations associated with these structures. For instance, nitrosoamines do not absorb above 1500 cm.$^{-1}$, whereas nitrones usually have one intense band in the 1570–1620-cm.$^{-1}$ region.[22] Thus structure II seems incompatible with the observed spectra.

The ultraviolet spectra of compounds V, VI, and VII are characterized by low intensity absorption (ϵ_{max} 500–600) at 270 mμ. This wave length must be associated with the pernitroso function, but the nature of the transition is unknown. The spectra are not compatible with those of nitrosamines,[23a] nitrones,[22] or nitrites[23a] ruling out structures I and II. The mesoionic structure (IV) would be expected to lead to a high intensity band.[23b] The nitrimine structure (III) would not *a priori* be expected to lead to the spectra observed for compounds V–VII, since they are quite unlike that of nitroolefins.[24] However, the differences in these spectra from those of nitroolefins are similar to the differences in the spectrum of furfuralnitrimine[14] (λ_{max} 270, ϵ_{max} 8000, λ_{max} 370, ϵ_{max} 800)[25] in which the long wave length band is of low intensity unlike that in the corresponding nitroolefin, 2-furylnitroethylene (λ_{max} 237, ϵ_{max} 4900, λ_{max} 350, ϵ_{max} 18700).[26]

Reduction. The behavior of these materials upon reduction with complex hydrides provided final proof of the nitrimine structure. Previously it has been reported that reduction of pernitrosocamphor (V) with aluminum amalgam produced a mixture of bornyl- and isobornylamines.[11] This result had at one time been used to argue for the existence of a C—N—O rather than a C—N—N linkage in pernitroso compounds.[27] Similarly the arguments for structure IV rested in part on these reduction products.[15] Recently, Horner[3b] has shown that catalytic reduction of benzophenone nitrimine proceeds by reduction to benzophenone imine and then to benzhydrylamine.

It has been shown that complex hydrides will reduce nitroolefins to nitroparaffins under carefully

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[12] R. Fusco and G. Trisoglio, *Atti accad. Italia, Rend., classe sci. fis. mat. nat.*, [7] **2,** 618, 751 (1941). These papers contain an excellent summary of the arguments for the various structures.

[13] R. Scholl, *Ann.*, **338,** 1 (1905).

[14] J. W. Suggitt, G. S. Myers, and G. F. Wright, *J. Org. Chem.*, **12,** 373 (1947).

[15] S. G. Brooks, R. M. Evans, G. F. H. Green, J. S. Hunt, A. G. Long, B. Mooney, and L. J. Wyman, *J. Chem. Soc.*, 4614 (1958). We are indebted to Dr. Long for bringing this article to our attention.

[16] J. P. Freeman, *Chemistry and Industry*, 1624 (1960).

[17] Since similar bands are reported in the infrared spectra of the steroid 20-nitrimines,[15] it may be assumed that they have similar structures.

[18] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77,** 634 (1955).

[19] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, 1958, p. 269. Aliphatic imines absorb in the range 1640–1690 cm.$^{-1}$

[20] Arguments similar to these have been used for the assignment of the nitrimine structure to the compounds obtained from the azine bisoxide-nitric oxide reaction[3b] [W. Kirmse, *Naturwissenschaften*, **46,** 379 (1959).] However, structure II was not considered.

[21] Ref. 19, p. 304.

[22] R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. R. Todd, *J. Chem. Soc.*, 2094 (1959).

[23a] R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 691 (1954).

[23b] W. Baker and W. D. Ollis, *Quart. Revs.* **11,** 15 (1957).

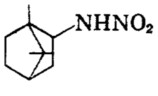
[24] E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

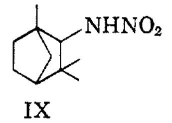
[25] R. N. Jones and G. D. Thorn, *Can. J. Research*, **27B,** 828 (1949).

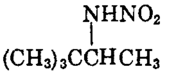
[26] That the imine and nitro groups are not conjugated in the conventional sense is reflected in the infrared spectra also. Thus the nitro group stretching frequencies are found in the same region as saturated C- and N-nitro compounds whereas in nitroolefins[18] this frequency is lowered to 1510–1540 cm.$^{-1}$ Haszeldine[23a] has stated that the unshared pair of electrons on the amino nitrogen of nitramines cannot interact with the nitro group but gives no reason for this inhibition. In these systems it appears that the nitrogen atom acts almost as an insulator to electron delocalization.

[27] A. Angeli and V. Castellana, *Atti. accad. Lincei*, [5] **14,** I, 669 (1905).

controlled conditions.[28] Reduction of V, VI, and VII with potassium borohydride in ethanol or with lithium aluminum hydride yielded the corresponding primary nitramines VIII, IX, and X. The stereochemistry of the reduction was not established so that the configurations of VIII

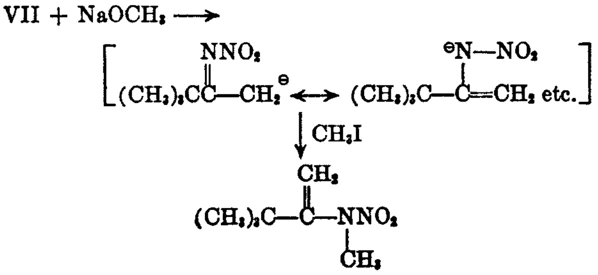

VIII


IX

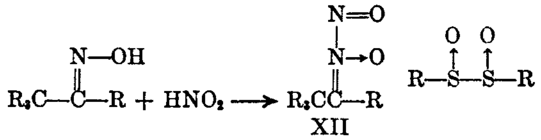

$$\overset{NHNO_2}{(CH_3)_3CCHCH_3}$$
X

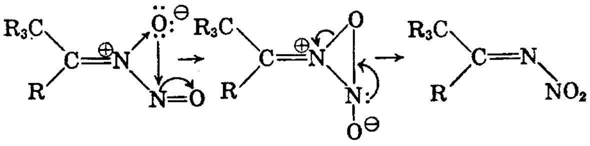
and IX are unknown. For convenience, they are referred to as bornylnitramine and fenchylnitramine, respectively. The structure of these compounds was established by elementary analysis, their infrared spectra (NH absorption at 3300 cm.$^{-1}$ and nitro group absorption at 1580 and 1330–1370 cm.$^{-1}$; no C=N absorption), ultraviolet spectra (λ_{max} 240, ϵ_{max} 8000)[29] and NMR spectra (N—H proton resonance at −125 c.p.s.).[30] In addition, treatment of bornylnitramine (VIII) with dilute sulfuric acid produced camphene, the product to be expected of the carbonium ion generated in this reaction.[31]

Isopernitroso compounds. Pernitroso compounds with α-methylene groups dissolve in alcoholic alkali to form salts.[32] In his original investigation on pernitrosopinacolone, Scholl[18] reported that it was converted to a salt by sodium methoxide and that this salt was alkylated by methyl iodide to form the vinylnitramine XI. Since this transformation bears directly on the structure of pernitroso compounds, the reaction was repeated and the product examined. Its spectral characteristics support the assigned structure XI. Its infrared spectrum showed strong bands at 1535 and 1280 cm.$^{-1}$ due to the nitro group, a sharp, weak band at 1650 cm.$^{-1}$ due to the double bond, and a medium band at 920 cm.$^{-1}$ due to the terminal methylene group. Its proton NMR spectrum[30] had signals at +217 c.p.s. (CH$_3$—C), +125 c.p.s. (CH$_3$—N), and a doublet at +48 and +55 c.p.s. (=CH$_2$).[33] This confirmation of structure XI lends further support to the nitrimine structure VII for pernitrosopinacolone.


XI

Formation. A major barrier to the acceptance of the nitrimine formulation has been in rationalizing the formation of a nitro group from the reactants. *N*-Nitrosation is a probable first step in the reaction. The resultant nitrosonitrone (XII) may be considered to be similar to a disulfoxide which apparently disproportionates intramolecularly to form a thiol sulfonate, RSO$_2$SR.[34] Oxygen transfer may occur through a three-membered ring and is probably favored by relief of steric strain and by the highly electrophilic nature of the nitroso group[35]:


XII



In the case of pernitrosomesityl oxide,[9] electrons are available from the double bond; and ring closure rather than oxygen migration occurs. The presence of the *t*-alkyl group probably is responsible for the stability of the pernitroso function toward hydrolysis. Attempts to prepare pernitroso compounds from norcamphor oxime and methyl cyclopropyl ketoxime yielded mixtures which contained the nitrimine function as indicated by their infrared spectra; all attempts at isolation led to hydrolysis.

EXPERIMENTAL

Reduction of pernitroso compounds. Bornylnitramine. A solution of 4 g. (0.02 mole) of pernitrosocamphor[36] in 100

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[28] H. Shechter, D. E. Ley, and E. B. Roberson, Jr., *J. Am. Chem. Soc.*, **78**, 4984 (1956).

[29] Nitramines show λ_{max} 240, ϵ_{max} 6000–9000.[22a]

[30] The NMR spectra were measured with a Varian Associates high resolution spectrometer, V-4300 B, using a 40-mc. probe. The spectra are reported in terms of displacement in cycles per second (c.p.s.) from the proton resonance of benzene, the external reference. Negative frequency displacements indicate resonances at lower field relative to the reference. The spectra were measured on 10% carbon tetrachloride solutions.

[31] J. Barrott, I. N. Denton, and A. H. Lamberton, *J. Chem. Soc.*, 1998 (1953).

[32] A. Angeli, *Atti. accad. Lincei*, [5] 4, II, 255 (1895).

[33] This splitting of the methylene resonance is another example of differential shielding of the protons by bulky β-substituents; *cf.* Sukh Dev, *Tetrahedron*, **9**, 1 (1960); L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959, p. 106.

[34] N. Marangelli, G. Modena, and P. E. Todesco, *Gazz. chim. ital.*, **90**, 1 (1960). Recent investigations cast some doubt on the universality of this mechanism; D. Barnard and E. J. Percy, *Chemistry and Industry*, 1332 (1960).

[35] The electrophilic character of the nitroso group is probably the critical factor. In the nitric oxide–azine dioxide reaction,[3b] an *N*-nitroso-oxime intermediate which rearranges to a nitrimine was postulated. Here steric factors do not appear to be important. There appear to be no authentic examples of *N*-nitrosonitrones.

[36] A. Angeli and E. Rimini, *Gazz. chim. ital.*, **26**, II, 34 (1896).

ml. of dry tetrahydrofuran was added to a slurry of 2 g. (0.026 mole) of lithium aluminum hydride in 150 ml. of dry tetrahydrofuran. This mixture was stirred overnight at room temperature and then was boiled under reflux for 2 hr. The mixture was poured on ice and hydrochloric acid, and the organic product was extracted with ether. After these extracts were washed and dried, they were concentrated to yield 2.7 g. (70%) of a yellow solid. Recrystallization from pentane produced white plates, m.p. 98–99°.

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.75; H, 9.11; N, 13.97.

Fenchylnitramine. To a solution of 9.8 g. (0.185 mole) of potassium borohydride in 100 ml. of ethanol was added 9.8 g. (0.05 mole) of pernitrosofenchone.[37] The mixture was boiled under reflux for 2 hr., then poured into dilute hydrochloric acid and extracted with methylene chloride. Concentration of the organic extracts left 4.2 g. (40%) of a white solid which crystallized from pentane, m.p. 107–108°.

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.27; H, 9.29; N, 14.06.

Pinacolylnitramine. A solution of 5.0 g. (0.0347 mole) of pernitrosopinacolone[38] in 15 ml. of ethanol was added slowly to 2.0 g. (0.036 mole) of potassium borohydride in 15 ml. of water. This addition was carried out at ice bath temperatures over a 1-hr. period because it was very exothermic. After the addition was complete, 10 ml. of water was added and the mixture was saturated with potassium carbonate. The mixture was extracted with methylene chloride. The organic product was isolated and distilled to yield 2.7 g. (53%) of a colorless oil, b.p. 80–82° (2 mm.), n_D^{20} 1.4672.

Anal. Calcd. for $C_6H_{14}N_2O_2$: C, 49.29; H, 9.65; N, 19.17. Found: C, 49.14; H, 9.53; N, 19.44.

Methyl-α-(t-butylvinyl)nitramine. To a solution of 1.6 g. (0.07 g.-atom) of sodium in 25 ml. of anhydrous methanol was added 9.35 g. (0.065 mole) of pernitrosopinacolone[38] dissolved in 25 ml. of dry methanol and 20.0 g. (0.14 mole) of methyl iodide at ice bath temperatures. After the addition, the ice bath was removed and the mixture stirred at room temperature for 15 min., then under reflux for 4 hr. Excess methyl iodide and methanol were removed by distillation, 50 ml. of water was added, and the mixture was extracted with ether. The dried ether extracts were concentrated, and the residue was freed of the last traces of solvent in a desiccator. There was obtained 4.1 g. (40%) of solid product that was crystallized from hexane, m.p. 35–37° (lit.[13] m.p. 39°).

HUNTSVILLE, ALA.

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[37] F. Tiemann and F. Mahla, *Ber.*, 29, 2807 (1896).

[38] R. Scholl and G. Born, *Ber.*, 28, 1361 (1895).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Rearrangement in Borate Pyrolysis

O. L. CHAPMAN AND G. W. BORDEN

Received March 27, 1961

Pyrolysis of the borates of 3,3-dimethyl-2-butanol, borneol, cyclohexylcarbinol, and cyclobutylcarbinol gives rearranged products in every case. The formation of rearranged products is not consistent with the previously proposed *cis*-elimination mechanism and is interpreted on the basis of ionization of the borate esters.

Borate pyrolysis has been shown to be a useful method for the preparation of olefins.[1-3] The pyrolysis proceeds satisfactorily at temperatures well below those required for acetate pyrolysis and comparable to those employed for xanthate pyrolysis. The reaction is simple to carry out and gives excellent yields of olefins. The preparation of the borate esters is straightforward and from the experimental viewpoint superior to the preparation of xanthate esters. Mechanistically, the reaction has been considered a *cis* elimination analogous to the acetate and xanthate pyrolyses.[1,2,4] Our interest in utilization of borate pyrolysis led to an investigation of the structural integrity of the reaction in systems prone to carbonium ion rearrangements. We have examined the products of pyrolysis of the borates of 3,3-dimethyl-2-butanol, borneol, cyclohexylcarbinol, and cyclobutylcarbinol. Rearranged products predominate (94–100%) in each case.

The experimental method employed in this study was that used by O'Conner and Nace.[1] Equimolar quantities of the alcohol and boric acid were warmed slowly to 120–140°, and the water which distilled was separated. The solid borate on further heating melted, then decomposed in the range 250–290°. The olefins which distilled were collected in a Dry Ice trap. The crude olefinic product was analyzed by vapor phase chromatography. The peak areas were read from the simultaneous trace of a mechanical integrator. Each product was separated by preparative scale vapor phase chromatography and identified by comparison of infrared absorption and vapor phase chromatographic retention time with an authentic sample.

Pyrolysis of the borate of 3,3-dimethyl-2-butanol (I) gave three olefins (92–96% yield) which were identified as 3,3-dimethyl-1-butene (II, 0.3%) 2,3-dimethyl-1-butene (III, 25.9%) and 2,3-dimethyl-2-butene (IV, 73.7%). Authentic 3,3-dimethyl-1-butene (II) was prepared by pyrolysis of 3,3-dimethyl-2-butyl acetate.[5] The product from

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[1] G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, 77, 1578 (1955).

[2] S. Dev, *J. Ind. Chem. Soc.*, 33, 769 (1956).

[3] W. Brandenberg and A. Galat, *J. Am. Chem. Soc.* 72, 3275 (1950).

[4] For an excellent review of *cis* eliminations see C. H. DePuy and R. W. King, *Chem. Revs.*, 60, 431 (1960).

[5] F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, 55, 1106 (1933).