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

Addition of Dinitrogen Tetroxide to Camphene and *trans*-Stilbene; the Effect of Oxygen

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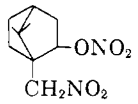
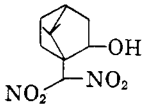
The reaction of camphene and *trans*-stilbene with dinitrogen tetroxide in the presence of oxygen and nitrogen as carrier gases has been investigated. When nitrogen was used as the carrier gas a mixture of 1,2-dinitrocompounds and 1,2-nitroalcohols was obtained from both olefins. The use of oxygen as the carrier gas led to the formation of α-nitroketones, 1,2-nitronitrates and 1,2-nitroalcohols but eliminated formation of the 1,2-dinitrocompounds.

Previous studies of the addition of dinitrogen tetroxide to olefins[1] have established that the reaction, when carried out in a weakly basic solvent such as ether, proceeds by a homolytic process. A β-nitroalkyl radical is produced by the addition of NO_2 to the olefin, and further reaction of this radical gives products. It also is known that conducting the dinitrogen tetroxide–olefin reaction in the presence of oxygen leads to a product distribution different from that obtained in the absence of oxygen.[1c,1e,2]

A study of the camphene–dinitrogen tetroxide reaction[3] initially was undertaken in conjunction with the camphene–dinitrogen pentoxide reaction.[4] Since 2-nitrato-10-nitrocamphane (I) was formed in the latter case and was shown to produce 2-hydroxy-10,10-dinitrocamphane (II) on base treatment followed by acidification,[4] it appeared probable that the dinitroalcohol II, originally isolated from the camphene-dinitrogen tetroxide reaction,[5] was not a primary product of this reaction but was formed from the nitronitrate I during the basic extraction of the reaction mixture.[5]

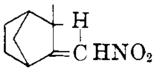


I

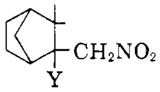


II

When an excess of dinitrogen tetroxide was added in a stream of dry nitrogen to an ether solution of camphene the products isolated were *dl*-ω-nitrocamphene (III), m.p. 64–65°, 3-(nitromethyl)-3-nitrocamphenilane (IVa), m.p. 141–143°, and 3-(nitromethyl)-3-hydroxycamphenilane (IVb), m.p. 37–39°. Compounds IVa and IVb were isolated in yields of 30 and 35%, respectively, while ω-nitrocamphene was formed in 5% yield. A trace of a nitrate ester, probably I, also was present in the reaction mixture. The nitroalcohol IVb (formed by hydrolysis of the nitronitrite IV, Y = –ONO) and the dinitro compound IVa correspond to the usual compounds obtained from the homolytic reaction of dinitrogen tetroxide and an olefin.[2]



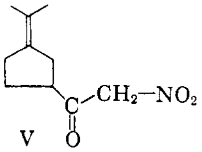
III



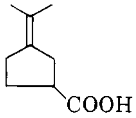
IVa, Y = -NO2
b, Y = -OH

Treatment of compounds IVa and IVb with aqueous ethanolic potassium hydroxide gave ω-nitrocamphene in yields of 59 and 56%, respectively. Similarly, base treatment of the crude camphene–dinitrogen tetroxide reaction mixture gave ω-nitrocamphene in about 40% yield.

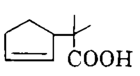
In the presence of oxygen as the carrier gas the camphene–dinitrogen tetroxide reaction gave a mixture of products that included 2-nitrato-10-nitrocamphane (I) and the α-nitroketone V, m.p. 76–77°. About 30% of the reaction mixture consisted of nitroacids whose structures have not been determined. The presence of IVa and/or IVb in the reaction mixture was indicated by the isolation of ω-nitrocamphene (6%) after treatment of a portion of the crude product with potassium hydroxide. The amount of nitronitrate I and nitroketone V formed varied somewhat from run to run (similar variations were found in the stilbene case, *vide infra*), but compound I was usually present to the extent of 3–6% while V appeared to form in 20–28% yield.



V



VI



VII

The structure of the nitroketone V was established by its base-catalyzed cleavage to 3-isopropylidenecyclopentanecarboxylic acid (VI), m.p. 50°. An acid of structure VI has been reported from the ozonolysis of camphene[6,7] and a comparison of the physical properties of VI and camphoceenic acid, formulated as VII,[8] has been made.[6] However, neither acid was obtained as a solid in the latter study[6] and a comparison of the properties of camphoceenic acid and the acid derived from V appeared worthwhile. The camphoceenic acid obtained by hydrolysis of the nitrile produced in the camphenilone oxime (VIII)–acetyl chloride reaction indeed was identical by mixed melting point and infrared spectrum with that obtained by hydrolysis

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[1] (a) H. Shechter and F. Conrad, THIS JOURNAL, **75**, 5610 (1953); (b) J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.*, 629 (1958); (c) J. F. Brown, Jr., personal communication; (d) T. E. Stevens and W. D. Emmons, THIS JOURNAL, **80**, 338 (1958); (e) A. N. Baryshnikova and A. I. Titov, *Doklady Akad. Nauk S.S.S.R.*, **91**, 1099 (1953) [*C. A.*, **48**, 10629 (1954)].

[2] N. Levy, C. W. Scaife, A. E. Wilder-Smith and H. Baldock, *J. Chem. Soc.*, 2627 (1949), and preceding papers.

[3] The results of which were reported as a communication, T. E. Stevens, *Chemistry & Industry*, 1546 (1957).

[4] T. E. Stevens, *J. Org. Chem.*, in press.

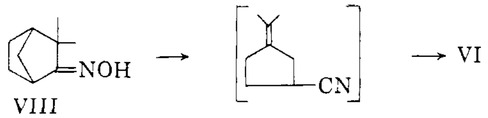
[5] P. Lipp, *Ann.*, **399**, 241 (1913).

[6] F. W. Semmler, *Ber.*, **42**, 246 (1909).

[7] P. S. Bailey, *ibid.*, **88**, 795 (1955).

[8] J. L. Simonsen, "The Terpenes," Vol. II, Cambridge University Press, Cambridge, England, 1950, p. 372.

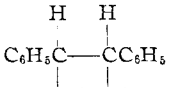
of the α-nitroketone V. Ozonolysis of the acid VI produced cyclopentanone-3-carboxylic acid and thus confirmed VI as the structure for camphoceenic acid. The n.m.r. spectra of the nitroketone V and camphoceenic acid (VI) also supported the structural assignments.

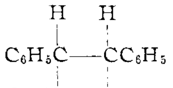


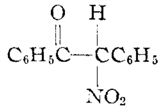
VIII

Since the experiments mentioned above offered additional[1e] indication of interaction between oxygen and the β-nitroalkyl radical in dinitrogen tetroxide–olefin reactions, the reaction of *trans*-stilbene and dinitrogen tetroxide in the presence of oxygen and nitrogen as carrier gases was examined. Earlier studies of the dinitrogen tetroxide–stilbene reaction[9] led to the isolation of the two α,α'-dinitrobibenzyls; the compound melting at 235° was shown to be the *meso* isomer while the isomer melting at 150° was assigned the *dl*-structure. Isolation of an α-hydroxy-α'-nitrobibenzyl from hydrolysis of the expected nitronitrites also was reported.[9]

Conducting the stilbene–dinitrogen tetroxide reaction by sweeping the tetroxide into an ether solution of stilbene with a stream of nitrogen has been found to yield, after hydrolysis of the nitronitrites, a mixture of the dinitrobibenzyls and the expected nitroalcohols. The *meso*-dinitrobibenzyl, m.p. 235–237°, was isolated in 20.8% yield; the *dl* (149°) isomer was obtained in 32.2% yield. The mixture of *threo*- and *erythro*-α-hydroxy-α'-nitrobibenzyls (IX) produced in the reaction in a crude yield of 28.8% was separated by chromatography on silica gel and gave compounds melting at 99° (10.4%) and 106° (12.6%). The isomer melting at 106° was assigned the *threo* configuration and the isomer melting at 99° the *erythro* configuration since the 106° isomer gave the known *dl-threo*-α-acetoxy-α'-nitrobibenzyl[10] on acetylation. If the nitroalcohols IXa and IXb were not separated by chromatography, material melting at 98–99° was obtained after recrystallization. These crystals appeared, from infrared analysis of the mixture of nitronitrates produced on nitration, to be a mixture of two parts IXa and one part IXb.


$$C_6H_5\underset{OH}{\overset{H}{C}}-\underset{NO_2}{\overset{H}{C}}C_6H_5$$
IXa, m.p. 106°
IXb, m.p. 99°


$$C_6H_5\underset{O_2NO}{\overset{H}{C}}-\underset{NO_2}{\overset{H}{C}}C_6H_5$$
Xa, m.p. 96°
Xb, m.p. 165°


$$C_6H_5\overset{O}{\overset{\|}{C}}-\underset{NO_2}{\overset{H}{C}}C_6H_5$$
XI

When oxygen was used as the carrier gas to sweep the dinitrogen tetroxide into the ether solution of stilbene there was obtained after the usual hydrolysis a quite different product mixture. No dinitro compound was isolated from the reaction; instead, a mixture of *threo*- and *erythro*-α-nitrato-α'-nitrobibenzyls (X), m.p.'s 96° and 165° respectively,[11] α-nitro-α-phenylacetophenone (XI), m.p. 75°, and the α-hydroxy-α'-nitrobibenzyls (IX) were obtained. A small amount of benzoic acid and benzaldehyde was formed also. Table I shows the crude yields of products obtained. The first three runs were carried out under essentially identical experimental conditions except that the addition of dinitrogen tetroxide, which took about an hour, was not controlled closely. It appears that minor differences in reaction conditions can cause an appreciable change in product composition.

TABLE I

PRODUCT YIELDS IN DINITROGEN TETROXIDE–STILBENE–OXYGEN REACTION

Product	Yield, %[a] Run I[d]	Run II[d]	Run III[d]	Run IV[e]
Stilbene (recovered)	1.6	1.8	0.4	52.8
Benzoic acid	7.4	[f]	[f]	1.8
Benzaldehyde[b]	1.1	1.0	[f]	0.9
α-Nitrato-α'-nitrobibenzyl[c]	24.9	15.9	12.3	5.4
α-Nitro-α-phenylacetophenone	24.2	31.4	32.6	14.8
α-Hydroxy-α'-nitrobibenzyl[c]	28.8	28.4	28.6	13.8

[a] Yields given here are crude yields obtained by chromatographic separation as outlined in the Experimental section and probably are maximum values. [b] Isolated as the 2,4-dinitrophenylhydrazone. [c] Mixture of *threo* and *erythro* compounds. [d] Runs I, II and III were carried out under the same experimental conditions except for the unknown variations in rate of addition of dinitrogen tetroxide. [e] Addition of 0.9 ml. (0.014 mole) of dinitrogen tetroxide to 5.0 g. (0.028 mole) of stilbene. [f] Component not isolated.

The *erythro*-α-nitrato-α'-nitrobibenzyl (Xb) predominated in the mixture of nitronitrates produced in the oxygen experiments; quantitative infrared analysis indicated the mixture was 65% *erythro*–35% *threo*. However, the α-hydroxy-α'-nitrobibenzyls were produced in about the same stereochemical ratio and the same yield in the presence of either nitrogen or oxygen. From the separation obtained on silica gel the nitroalcohol mixture from the nitrogen experiment (28.8%) was 56% *threo*, while that from the oxygen experiment (Table I, run III, 28.6%) was 59% the *threo* isomer.

The structure of α-nitro-α-phenylacetophenone was confirmed by heating the compound under reflux in ethanolic sodium hydroxide; benzoic acid and phenylnitromethane were produced.

The products obtained when these olefin–dinitrogen tetroxide reaction were carried out in the presence of nitrogen can be explained by the usual mechanism,[1a,1b] *i.e.*, reaction of the intermediate β-nitroalkyl radical with NO_2 or N_2O_4 to give either dinitro compound or nitronitrite. Hydrolysis of the latter gives rise to the nitroalcohols. Rationalization of the results of the oxygen experiments is more difficult, but probably involves interaction of oxygen and the β-nitroalkyl radical. It has been shown that the β-nitroalkyl radical produced in the dinitrogen tetroxide–olefin reaction will react with iodine to give high yields of β-nitroalkyl iodides[1d] or with bromotrichloromethane to give β-nitroalkyl

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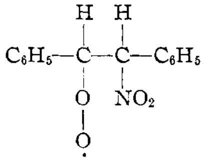
[9] J. Schmidt, *Ber.*, **34**, 3536 (1901); J. J. Gardikes, A. H. Pagano and H. Shechter, *Chemistry & Industry*, 632 (1958).

[10] G. Drefahl and H. Crahmer, *Ber.*, **91**, 745 (1958).

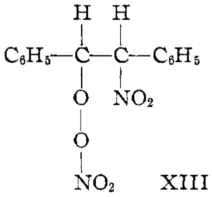
[11] Nitration of the *dl-threo*-α-hydroxy-α'-nitrobibenzyl, m.p. 106°, with dinitrogen pentoxide produced the α-nitrato-α'-nitrobibenzyl of m.p. 96°; hence, this nitronitrate was assigned the *dl-threo* configuration. The nitronitrates Xa and Xb were first isolated from the dinitrogen pentoxide–stilbene reaction, T. E. Stevens, *J. Org. Chem.*, in press.

bromides.[1b] Despite the fact that carbon radicals appear to react readily with oxygen,[12] almost no consideration has been given to the possibility of this interaction occurring when dinitrogen tetroxide and an olefin react in the presence of oxygen.[13,14]

Thus, it appears reasonable to assume that, when a relatively stable radical such as the nitroalkyl radical of stilbene, styrene or camphene is formed in the presence of a large excess of oxygen, intermediates such as the nitroperoxy radical XII or the nitroperoxynitrate XIII may be formed. The results of run IV, Table I, show that dinitrogen tetroxide is consumed in some further reaction of the nitroalkyl radical, but the nature of this process is obscure. There are several paths by which intermediates such as XII or XIII could yield the products actually isolated; the merits of these processes will be discussed in another publication.[13]


$C_6H_5-CH(O-\dot{O})-CH(NO_2)-C_6H_5$

XII


$C_6H_5-CH(O-O-NO_2)-CH(NO_2)-C_6H_5$

XIII

Experimental

Melting points are uncorrected. Dinitrogen tetroxide was obtained from the Matheson Co. and was redistilled before use. All stilbene used was the *trans* form; camphene was obtained from Eastman Kodak Co. and fractionated before use.

Reaction of Camphene and Dinitrogen Tetroxide.—A solution of 10.0 g. (0.073 mole) of camphene in 300 ml. of dry ether was cooled in an ice-bath while 0.10 mole of dinitrogen tetroxide was swept into the stirred solution in a stream of dry nitrogen over 2 hours. After the addition of the dinitrogen tetroxide the solution was stirred for 30 minutes. The reaction mixture then was quenched in aqueous sodium bicarbonate, and the organic layer was separated and washed with water and dried over magnesium sulfate. The oily residue remaining on evaporation of the ether weighed 15.1 g. A 7.5-g. portion of this residue in 150 ml. of 50% ethanol containing 10.0 g. of potassium hydroxide was stirred for two hours. The solution was cooled, acidified with cold 10% sulfuric acid and extracted with ether. The residue from the ether, 5.9 g., was chromatographed on silica gel to give ω-nitrocamphene (III), 2.46 g. (37.3%), m.p. 64–65°.

A 7.2-g. portion of the original reaction residue was extracted with hot ligroin to leave 0.2 g. of insoluble residue. Chromatography of the ligroin extract was carried out on a Celite-silicic acid (1:1) column. Elution of the column with ligroin gave 0.35 g. of ω-nitrocamphene, m.p. 60–62°, and 0.20 g. of material whose infrared spectrum indicated it was a mixture of ω-nitrocamphene and 2-nitrato-10-nitrocamphane (I). Continued elution of the column with ligroin containing increasing amounts of ether gave 0.33 g. of 3-(nitromethyl)-3-hydroxycamphenilane (IVb). The 3.31-g. intermediate cut was taken up in benzene–ligroin (1:1) and chromatographed on silica gel. Elution of the column with benzene gave 2.04 g. of IVa; elution of the column with methylene chloride containing 10% ethyl acetate gave an additional 1.04 g. of IVa. After recrystallization from ligroin the 3-(nitromethyl)-3-nitrocamphenilane was a white, waxy solid, m.p. (hot-stage) 141–143°.

Anal. Calcd. for $C_{10}H_{16}N_2O_4$: C, 52.62; H, 7.07; N, 12.27. Found: C, 52.53; H, 7.31; N, 11.13.

The 3-(nitromethyl)-3-hydroxycamphenilane melted at 37–39° after recrystallization from ligroin.

Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.23; H, 8.60; N, 7.03. Found: C, 60.26; H, 8.78; N, 6.40.

Reaction of Camphene, Dinitrogen Tetroxide and Oxygen.—A solution of 10.0 g. (0.073 mole) of camphene in 300 ml. of dry ether was cooled in an ice-bath while 0.090 mole of dinitrogen tetroxide was swept into the stirred solution by an oxygen stream (1 cu. ft./hr.) over a 2-hour period. After addition of the dinitrogen tetroxide the solution was stirred for one hour in the oxygen stream. The ether solution was washed with water, 10% aqueous sodium bisulfite (twice) and water and was dried over magnesium sulfate. The residue obtained on removal of the ether weighed 14.9 g. A 7.4-g. portion of this residue was taken up in methylene chloride and washed with aqueous sodium bicarbonate and water. These washes were neutralized with hydrochloric acid and re-extracted to give 2.4 g. of acidic material. The infrared spectrum indicated the major product was a microacid(s). The fraction has not been characterized as yet. The methylene chloride was removed from the organic layer, and the residue was stirred for one hour with 150 ml. of 50% ethanol containing 6.0 g. of potassium hydroxide. The residue obtained after acidification (cold 15% sulfuric acid) and ether extraction was taken up in benzene and chromatographed on silica gel to give 0.37 g. (5.6%) of ω-nitrocamphene, m.p. 62–63°.

A 6.7-g. fraction of the original reaction residue was dissolved in ligroin–benzene (2:1) and chromatographed on silica gel. The first fraction eluted, 0.54 g., was recrystallized twice from ligroin to give 2-nitrato-10-nitrocamphane, 0.22 g. (2.7%) (I), m.p. 98–99°, reported[4] 98–99°. Continued elution of the column with methylene chloride gave 3-isopropylidenecyclopentyl nitromethyl ketone (V), 1.57 g. (24%), m.p. 76–77° after ligroin recrystallization.

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.66; N, 7.10. Found: C, 60.57; H, 7.64; N, 6.81.

The piperidinium salt, prepared by adding a slight excess of piperidine to an ether solution of the ketone, melted at 118–119°.

Anal. Calcd. for $C_{15}H_{26}N_2O_3$: C, 63.88; H, 9.20. Found: C, 63.80; H, 9.28.

The ultraviolet spectrum of V in ethanol exhibited λ_{sh} 230 mμ, ϵ 3,200, and λ_{max} 316 mμ, ϵ 660; in 50% ethanol–50% 0.1 *N* sodium hydroxide it had λ_{max} 234 mμ, ϵ 4,500, and λ_{max} 331 mμ, ϵ 19,600.

Continued elution of the column gave an additional 2.73 g. of material of which 1.94 g. was predominantly nitroacids whose infrared spectrum was very similar to those extracted by sodium bicarbonate (above).

Conversion of 3-(Nitromethyl)-3-nitrocamphenilane to ω-Nitrocamphene.—A 1.01-g. sample of 3-(nitromethyl)-3-nitrocamphenilane was stirred for 30 minutes in 30 ml. of 50% ethanol containing 0.5 g. of potassium hydroxide. The cold mixture was acidified with 10% sulfuric acid and extracted with ether. The residue from the ether extract was taken up in ligroin–benzene (1:1) and chromatographed on silica gel. Elution with the same solvent gave 0.47 g. (59%) of ω-nitrocamphene, m.p. 63–64°.

Conversion of 3-(Nitromethyl)-3-hydroxycamphenilane to ω-Nitrocamphene.—A 1.06-g. sample of 3-(nitromethyl)-3-hydroxycamphenilane was treated with ethanolic potassium hydroxide as above. There was obtained 0.54 g. (56%) of ω-nitrocamphene, m.p. 62–63°.

Hydrolysis of 3-Isopropylidenecyclopentyl Nitromethyl Ketone.—Three grams of the α-nitroketone V was dissolved in 30 ml. of ethanol–30 ml. of 10% sodium hydroxide and the solution was refluxed in an atmosphere of nitrogen for 3 hours. The solution was cooled, acidified with sulfuric acid and extracted with ether. The residue from the ether extract was taken up in methylene chloride and chromatographed on silica gel. The material eluted by 2% ethyl acetate in methylene chloride was recrystallized from aqueous ethanol to give 2.15 g. of camphoceenic acid (VI), m.p. 49–50°. The m.p. was 50–51° after further recrystallization from the same solvent.

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(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 169, 398.

(13) A forthcoming publication by J. F. Brown, Jr., will discuss the dinitrogen tetroxide–oxygen–olefin reaction in detail.[1c]

(14) The sequence nitroalkyl radical, nitroalkyl peroxy radical, nitroalkyl peroxy nitrate and heterolytic decomposition of the latter to give nitro ketone has been proposed to explain the formation of ω-nitroacetophenone in the styrene–oxygen–dinitrogen tetroxide reaction.[1e]

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.42; H, 9.39. Found: C, 70.10; H, 9.15.

Preparation of Camphoceenic Acid.—Camphenilone was prepared from ω-nitrocamphene by refluxing with ethanolic aqueous potassium hydroxide. The oxime, m.p. 106–107°, was prepared by refluxing camphenilone, hydroxylamine hydrochloride and potassium hydroxide in ethanol for 14 hours. The oxime, 1.7 g., was dissolved in 12 ml. of acetyl chloride, and the solution warmed to reflux, then allowed to cool to ambient temperature. After 3 hours methylene chloride was added, and the mixture treated with water. After hydrolysis the organic layer was separated, washed twice with water, dried over magnesium sulfate and taken to dryness. The residue was refluxed 4 hours with 30 ml. of 50% ethanol containing 2 g. of potassium hydroxide. The solution was cooled, acidified and extracted with ether. The residue obtained from the ether extract was taken up in methylene chloride and chromatographed on silica gel. The material eluted by 10% ethyl acetate in methylene chloride melted at 49–50° (reported[15] 54°) after recrystallization from aqueous ethanol. The infrared spectrum was identical with that of the acid from the α-nitroketone V, and the m.p. of a mixture of this acid and that derived from the hydrolysis of V was 49–50°. Another fraction from the column, eluted with 10% methanol in methylene chloride, melted at 152–154° and had the infrared spectrum and ultimate analysis expected for camphoceenic amide, reported[15] m.p. 155°.

Ozonolysis of Camphoceenic Acid.—A solution of 1.4 g. of camphoceenic acid in 50 ml. of methylene chloride was cooled to −40°, and ozonized oxygen was passed into the stirred solution until a pale color was evident and the exit gases oxidized acidified potassium iodide. The methylene chloride was removed at reduced pressure, and the residue was stirred one hour at 75° with 50 ml. of water. The aqueous solution was made basic with sodium hydroxide, extracted with ether (discarded), acidified with hydrochloric acid and extracted with ether. The residue from the ether extract was taken up in methylene chloride and chromatographed on silica gel. The major fraction, eluted by methylene chloride–ethyl acetate (3:1), was recrystallized twice from ligroin–benzene to give cyclopentanone-3-carboxylic acid, m.p. 60–62°, reported[16] 64–65°. The ultimate analysis confirmed the structure of the ketoacid.

Reaction of Stilbene and Dinitrogen Tetroxide under Nitrogen.—A stirred solution of 5.0 g. (0.028 mole) of stilbene in 250 ml. of anhydrous ether was maintained at 0–5° with an ice-bath while 2.3 ml. (0.036 mole) of dinitrogen tetroxide was added in a stream of dry nitrogen over a one-hour period. The reaction was stirred for one hour at the same temperature after addition of the dinitrogen tetroxide. The mixture then was filtered to remove an insoluble solid, and the filtrate was washed with water and aqueous sodium bicarbonate and was dried over magnesium sulfate. One recrystallization of the solid from chloroform gave 1.37 g. of *meso*-α,α′-dinitrobibenzyl, m.p. 235–237° dec. (reported[9] 235–236°). The chloroform filtrate was combined with the ethereal filtrate, and the solvent was removed at reduced pressure to leave a gummy residue. The residue was dissolved in a small amount of methylene chloride and chromatographed on a 2.8 × 34 cm. silica gel column using the listed solvents as eluent: 100 ml. of ligroin, 700 ml. of 3:1 ligroin–methylene chloride, 700 ml. of 1:1 ligroin–methylene chloride, 800 ml. of methylene chloride, 600 ml. of 49:1 methylene chloride–ethyl acetate and 500 ml. of 9:1 methylene chloride–ethyl acetate. A total of 5.47 g. of material was recovered from the column. The first fraction eluted was stilbene, 0.28 g. (5.6%). Recrystallization of the next fraction from ligroin yielded an additional 0.20 g. of the insoluble *meso*-α,α′-dinitrobibenzyl, m.p. 222–223° dec. (total of 1.57 g., 20.8%) and 2.11 g. of the *dl*-α,α′-dinitrobibenzyl, m.p. 149–151° (reported[9] 150–152°). A final crop, 0.33 g., m.p. 137–142°, of less pure, *dl*-dinitro compound was obtained also (total of 2.44 g., 32.2%). The third fraction from the column, 0.18 g., showing weak carbonyl and strong nitro group absorption in its infrared spectrum was discarded. The fourth fraction, 0.85 g., was recrystallized from ligroin to give *erythro*-α-hydroxy-α′-nitrobibenzyl (IXb), 0.70 g. (10.4%), m.p. 99–100°.

Anal. Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.31; H, 5.23; N, 5.67.

The acetate of the alcohol was prepared by allowing 0.30 g. of the nitroalcohol to stand overnight with 4.0 ml. of acetic anhydride and one drop of concentrated sulfuric acid. Recrystallization from ligroin of the residue obtained after hydrolysis of the excess acetic anhydride gave *erythro*-α-acetoxy-α′-nitrobibenzyl, 0.33 g. (94%), m.p. 115.5–116.5°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 68.01; H, 5.50; N, 4.92.

The last fraction from the column, 1.08 g., was recrystallized from ligroin to give *threo*-α-hydroxy-α′-nitrobibenzyl (IXa), 0.85 g. (12.6%), m.p. 105.5–106.5°. Further recrystallization from ligroin raised the m.p. to 106–107°.

Anal. Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.12; H, 5.27; N, 5.69.

The *threo*-α-acetoxy-α′-nitrobibenzyl was prepared as above in 91% yield, m.p. 136–137°, reported[10] 135°.

When the reaction was conducted as above except that a mixture of 80 ml. of ether–80 ml. of methylene chloride was used as the solvent, the yields were 18.8% of the *meso*-dinitro compound, 28.8% of *dl*-dinitro compound, and 34.2% of crude, mixed nitroalcohols.

If the nitroalcohols were not effectively separated on the chromatographic column (the separation usually occurred with G. F. Smith silica gel, but was never successful with Davison Grade 12 silica gel), recrystallization of the mixture led to crystals, m.p. 98–99°. These crystals depressed the m.p. of the *erythro*-nitroalcohol to 87–92° on admixture, but a mixed m.p. with the *threo*-nitroalcohol was 97–102°. Nitration of this material with dinitrogen pentoxide (described below) and quantitative infrared analysis of the mixture of α-nitro-α′-nitratobibenzyls produced indicated the crystals were a 2:1 *threo–erythro* mixture.

Reaction of Stilbene and Dinitrogen Tetroxide under Oxygen.—The reaction was conducted in the same manner and with the same quantities of materials (5.0 g. of stilbene, 2.3 ml. of dinitrogen tetroxide) as described above for the nitrogen experiment except that oxygen at a flow rate of 1.0 cu. ft./hr. was used to carry the dinitrogen tetroxide into the ether–stilbene mixture. The ether solution was washed successively with water, aqueous sodium bisulfite, water, aqueous sodium bicarbonate and water, and was dried over magnesium sulfate. Most of the benzoic acid reported in Table I was isolated from the bicarbonate washes by neutralization and re-extraction. The ether was removed at reduced pressures, and the residue, when benzaldehyde was isolated, was distilled into a Dry Ice cooled trap at 1 mm. and 25°. The benzaldehyde then was isolated from the cold trap at its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 233–235°. The residue then was dissolved in methylene chloride and chromatographed as described for the nitrogen run except that 700 ml. of ligroin was used as initial eluent and 500 ml. of methylene chloride–methanol, 9:1, was added as a final eluent. The workup of run III, Table I, is described below. The first fraction eluted was stilbene, 0.02 g., identified by m.p. and mixed m.p. The second fraction,[17] a mixture of the α-nitrato-α′-nitrobibenzyls X, 0.98 g., was assayed by its infrared spectrum and found to consist of 35% of the *threo*-nitronitrate. Recrystallization of the third fraction, 2.18 g., from ligroin gave α-nitro-α-phenylacetophenone (XI), 1.60 g., 24%, m.p. 74–75°, melting at 75–75.5° after further recrystallization from ligroin.

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.69; H, 4.59; N, 5.80. Found: C, 69.91; H, 4.79; N, 6.03.

The fourth fraction, 0.79 g., *erythro*-α-hydroxy-α′-nitrobibenzyl, was recrystallized from ligroin to give 0.39 g. (5.8%), m.p. 98–99°. Recrystallization of the next fraction, 1.13 g., from ligroin gave *threo*-α-hydroxy-α′-nitrobibenzyl, 0.70 g. (10.4%), m.p. 105–106°. The last fraction was recrystallized from ligroin–benzene to give benzoic acid, 0.05 g., m.p. and mixed m.p. 121–122°.

Hydrolysis of α-Nitro-α-phenylacetophenone.—A solution of 0.35 g. of α-nitro-α-phenylacetophenone in 25 ml. of

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[15] W. Jagelki, *Ber.*, **32**, 1498 (1899).

[16] F. W. Kay and W. H. Perkin, Jr., *J. Chem. Soc.*, **89**, 1640 (1906).

[17] Recrystallization of the nitronitrate fraction of run 1 (1.99 g.) from ligroin gave 0.97 g. of *erythro*-α-nitrato-α′-nitrobibenzyl, m.p. 157–160°. Evaporation of the filtrate and three recrystallizations from ligroin gave *threo*-α-nitrato-α′-nitrobibenzyl, m.p. 85–96°, 0.45 g., 84% pure by infrared analysis.

ethanol containing one ml. of 20% aqueous sodium hydroxide was refluxed for 2 hours in an atmosphere of nitrogen. The solution was cooled, poured into 100 ml. of water, neutralized with acetic acid, and the aqueous solution was extracted with ether. The residue remaining after evaporation of the ether was taken up in benzene and chromatographed on silica gel. Elution of the column with benzene gave 0.06 g. of phenylnitromethane, identified by infrared spectrum; elution of the column with methylene chloride containing 10% methanol gave benzoic acid, 0.15 g., m.p. and mixed m.p. 120–122°.

Nitration of Mixed Crystals of *threo*- and *erythro*-α-Hydroxy-α'-nitrobibenzyl.—A 1.46-g. sample of the mixed nitroalcohols, m.p. 98–99°, was nitrated with dinitrogen pentoxide as described previously.[11] There was obtained 1.63 g. (94%) of product, m.p. 80–108°, which assayed 67% *threo*-α-nitrato-α'-nitrobibenzyl from its infrared spectrum.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

On the Mechanism for the Oxo Reaction[1]

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When an excess of 1-hexene is added to a hexane solution of cobalt hydrocarbonyl at room temperature in the presence of one atmosphere of carbon monoxide, approximately one mole of gas is absorbed for every two moles of $HCo(CO)_4$. The rate of gas absorption with various olefinic substrates parallels the relative rates with which the respective olefins undergo hydroformylation. Aldehydes and dicobalt octacarbonyl can be isolated from the reaction mixture. Conjugated diolefins fail to absorb carbon monoxide. On the basis of the observed phenomena, a reaction scheme for the oxo synthesis is proposed.

Very careful studies in a number of laboratories have established that the rate of the oxo reaction is inversely proportional to the partial pressure of carbon monoxide. In accordance with this kinetic requirement, the usual mechanisms suggested for this reaction involve, as a rate-determining step, the displacement by the olefin of a mole of carbon monoxide from the dicobalt octacarbonyl[3–5] added as catalyst, or from the cobalt hydrocarbonyl[6] presumed to be present in the system.

Previous work in this Laboratory[7] showed that under oxo conditions, rapid conversion of dicobalt octacarbonyl to cobalt hydrocarbonyl occurred. In the presence of olefin, no free hydrocarbonyl could be detected but when the hydroformylation was complete and all the olefin consumed, the hydrocarbonyl again appeared uncombined. Because these results clearly showed that olefin–hydrocarbonyl interaction probably by complex formation is the essential catalytic step in the oxo synthesis, attention has been focused on the reaction between olefins and cobalt hydrocarbonyl.

Dilute solutions of cobalt hydrocarbonyl were prepared from hydrocarbon solutions of dicobalt octacarbonyl at 25° under one atmosphere of carbon monoxide by disproportionation[8] with dimethylformamide (DMF) and subsequent acidification of the resulting mixture according to the equations

$$3Co_2(CO)_8 + 12DMF \longrightarrow 2Co(DMF)_6[Co(CO)_4]_2 + 8CO \quad (1)$$

$$Co(DMF)_6[Co(CO)_4]_2 + 2HCl \longrightarrow 2HCo(CO)_4 + CoCl_2 + 6DMF \quad (2)$$

Removal of the acid–DMF phase left a clear yellow solution of cobalt hydrocarbonyl. Addition of excess olefin resulted in *absorption* of one mole of carbon monoxide for each two moles of hydrocarbonyl present. The disappearance of hydrocarbonyl proceeded simultaneously with the absorption of carbon monoxide. Terminal olefins absorbed carbon monoxide faster than internal olefins; the same order of reactivity has been noted[5] in the oxo reaction. If the acid phase is not removed prior to olefin addition, decomposition occurs and carbon monoxide is liberated.

After a number of orienting trials, the following procedure was used in one particular experiment. The clear yellow solution of hydrocarbonyl in hexane was prepared as above. The infrared absorption spectrum of a small aliquot of the solution was determined. The solution spectrum of the hydrocarbonyl was essentially identical with its reported vapor spectrum and showed the absence of dicobalt octacarbonyl. To the balance of the solution, there was added excess 1-hexene. After one mole of carbon monoxide per two moles of hydrocarbonyl had been absorbed, absorption ceased (10 min.). The reaction flask was cooled to Dry-Ice temperature whereupon bright orange crystals of dicobalt octacarbonyl (melting point, infrared spectrum) separated in about 80% yield. The infrared spectrum of the filtrate showed: the absence of appreciable dicobalt octacarbonyl; sharp bands in the 4.8–4.9 μ region which were not identical with either octacarbonyl or hydrocarbonyl; the presence of 1-hexene; the presence of internal olefins; the presence of aldehydes. Gas chromatographic analysis indicated that about 35% of the unreacted olefin was 2-hexene and/or 3-hexene. Treatment of the reaction mixture with 2,4-dinitrophenylhydrazine gave a mixture of hydrazones whose analysis was consistent with heptaldehyde 2,4-dinitrophenylhydrazine.

It is clear from the above evidence that the room temperature hydroformylation of 1-hexene must be

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(1) For a preliminary communication on this subject see L. Kirch and M. Orchin, THIS JOURNAL, **80**, 4428 (1958).

(2) Taken in part from this author's dissertation submitted to the graduate faculty of the University of Cincinnati in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(8) I. Wender, H. Sternberg and M. Orchin, *ibid.*, **74**, 1216 (1952).