phenyl-*m*-xylylene glycol was prepared by hydrolysis of a 98% sulfuric acid solution of the corresponding dichloride which in turn was obtained by treatment of the crude glycol from dimethyl isophthalate and phenylmagnesium bromide with acetic acid–acetyl chloride–hydrogen chloride.[51] The glycol, after recrystallization from 90–120° ligroin, melted sharply at 87°; evacuation overnight in a drying pistol gave solvent-free glycol, m.p. 112–113°.[53] Tetraphenyl-*o*-xylylene glycol, m.p. 203–204°, was obtained from dimethyl phthalate and phenyllithium.[47] Tetraphenylphthalan, m.p. 174–176° from acetic acid, was obtained by refluxing the *o*-glycol with glacial acetic acid containing a little water.[47] Tetra-*p*-anisyl-*p*-xylylene glycol, m.p. 167–168° from acetone, was obtained from dimethyl terephthalate and *p*-methoxyphenylmagnesium bromide.[27] α,α′-Diphenyl-*p*-xylylene glycol, m.p. 173° from ethanol, was obtained from terephthalaldehyde and phenylmagnesium bromide.[52] The *m*-isomer was obtained by reduction of *m*-dibenzoylbenzene with lithium aluminum hydride in ether–benzene; recrystallized from toluene–ligroin (90–120°), m.p. 153–155°.[54]

Hydrolysis and Methanolysis Experiments.—The deep red solution of 1.5 g. of tetraphenyl-*p*-xylylene glycol in 15 ml. of 100% sulfuric acid was poured onto 100 g. of ice. The white precipitate, taken up in ether, was washed with water, 5% sodium bicarbonate, dried, and the solvent removed (air stream), yielding 1.38 g. (92%) of recovered glycol, m.p. and m.m.p. 169–170°.

A solution of 2.0 g. of tetraphenyl-*p*-xylylene glycol in 50 ml. of methanol containing 2 drops of concentrated sulfuric acid was refluxed for 2 hours (white crystals began to deposit almost immediately). The crystals were filtered and recrystallized from benzene–petroleum ether (60–90°), yielding 1.8 g. (87%) of the dimethyl ether, m.p. 185°.[23]

The red solution of 0.1 g. (0.21 mmole) of tetraphenyl-*m*-xylylene dichloride in 5 ml. of 98% sulfuric acid was added to 50 ml. of ice-cold methanol. The resulting colorless solution was treated with 50 ml. of 5% sodium carbonate, and the resulting white solid was filtered and recrystallized from aqueous methanol, yielding 0.08 g. (82%) of the corresponding dimethyl ether, m.p. 103°.[53]

The orange-red solution of 1.19 g. (2.7 mmoles) of tetraphenyl-*o*-xylylene glycol in 10 ml. of 98% sulfuric acid was poured onto 50 ml. of ice-water. The white solid was taken up in benzene, washed with 5% sodium carbonate, then water, dried (calcium chloride) and the solvent removed *in vacuo*, to give 0.960 g. (84%) of tetraphenylphthalan, m.p. and m.m.p. 173–174° from benzene.

A solution of 1.00 g. (2.25 mmoles) of tetraphenyl-*o*-xylylene glycol in 10 ml. of 98% sulfuric acid was added to 75 ml. of ice-cold absolute methanol. The white solid was washed with 5% sodium carbonate, water, and dried giving 0.885 g. (89%) of 9 - methoxy - 9,10,10 - triphenyl - 9,10 - dihydroanthracene, m.p. 220.5–221° after recrystallization from benzene–ligroin (90–120°).[39] A completely analogous procedure using ethanol in place of methanol gave an 84% yield of 9-ethoxy-9,10,10-triphenyl-9,10-dihydroanthracene, m.p. 254–255°[39] from toluene–ligroin (90–120°). The structure of the 9-methoxy compound is clear not only from its m.p., analysis, formation of the analogous 9-ethoxy compound whose m.p. is also known, but also by the following experiment. The 9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene (1.00 g., 2.3 mmoles) was dissolved in 10 ml. of 98% sulfuric acid, and the resulting red solution poured onto 50 ml. of ice-water. The resulting white solid, washed with sodium carbonate, water, and dried, gave 0.80 g. (83%) of the known 9,10,10-triphenyl-9,10-dihydro-9-anthrol, m.p. 204–204.5° from ligroin (90–120°).[40]

To a magnetically stirred orange-red solution of 0.150 g. (0.34 mmole) of tetraphenyl-*o*-xylylene glycol in 50 ml. of 98% sulfuric acid there was added dropwise 50 ml. of absolute methanol. The color lightened slowly with the formation of a white solid. When addition was complete, the solid was filtered, washed with water, sodium carbonate, water, and dried at 100°. The product, m.p. and m.m.p. with tetraphenylphthalan 175–176°, weighed 0.120 g. (80%).

The cherry-red solution of 2.0 g. of tetra-*p*-anisyl-*p*-xylylene glycol in 15 g. of 100% sulfuric acid was poured onto 100 g. of ice. The white solid was taken up in ether, washed with water, sodium carbonate, water, and dried over magnesium sulfate. Evaporation of the ether gave 1.79 g. (90%) of recovered (m.p. and m.m.p.) glycol.

Cryoscopic Procedure.—The apparatus has been described.[2a] The initial freezing point of sulfuric acid was checked at 2-hour intervals to see that it remained constant ±0.005° before solute was added. The solute was added as solid, using a special addition funnel which delivered the solid as powder, close to the sulfuric acid surface. The weight of sample was determined by difference weighings on the delivery funnel. In order to eliminate errors such as freezing too rapidly or too slowly (with Dry Ice initiation of nucleation) or improper stirring, the solute–acid mixture was melted and refrozen 4 or 5 times; the mean freezing point depression was used.

Spectra.—Stock solutions of aqueous sulfuric acid of varying strengths were analyzed by titration with sodium hydroxide to phenolphthalein end-point. Sulfuric–acetic acid solutions were prepared according to Hall and Spengeman.[42] Solutions for pK_R studies were prepared by dissolving a known weight of carbinol in 25 ml. of glacial acetic acid[54] and diluting 0.100 ± 0.001 ml. of this solution to 10 ml. with sulfuric acid of appropriate strength. The small sample was delivered from a La Pine 0.50-ml. microburet.

Spectra were recorded on a Cary 11 spectrophotometer, using 1-cm. glass-stoppered quartz cells; earlier experiments were done on a Beckman DK-2 instrument.

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(51) W. Schlenk and M. Brauns, *Chem. Ber.*, **48**, 661 (1915).

(52) R. Deluchat, *Compt. rend.*, **190**, 438 (1930).

(53) O. Stark and O. Garben, *Chem. Ber.*, **46**, 2252 (1913).

(54) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 281.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY, COLUMBUS, O.]

The Stereochemistry of Liquid-Phase Nitration of (+)-3-Methylheptane, *cis*- and *trans*-Decalins and *cis*- and *trans*-Hydrindanes

BY HAROLD SHECHTER AND DEVIN K. BRAIN[1]

RECEIVED DECEMBER 11, 1962

Liquid-phase nitration of (+)-3-methylheptane yields racemic 3-methyl-3-nitroheptane; the stereochemistry of the nitro compound was confirmed upon its conversion to optically inactive 3-amino-3-methylheptane and N-phenyl-N′-3-(3-methylheptyl)-thiourea. Reactions of *cis*- and *trans*-decalins, respectively, with aqueous nitric acid give *trans*-9-nitrodecalin as the principal tertiary nitration product (>77–86.5%); the composition and stereochemistry of the 9-nitrodecalin were determined upon its conversion to *trans*-9-aminodecalin and to *trans*-N-9-decalylacetamide. *trans*-9,10-Dinitrodecalin is also formed in nitration of *cis*- or *trans*-decalins. Nitrations of *cis*- and *trans*-hydrindanes yield 8-nitrohydrindanes of near-identical stereochemistry and composition. The stereochemistries of liquid-phase nitrations are interpreted in terms of hydrocarbon radical intermediates.

Saturated hydrocarbons react with nitric acid or nitrogen dioxide in the liquid phase to give nitro compounds along with nitrates, carbonyl derivatives and various oxidation and polynitration products. Liquid-phase nitrations of alkanes, cycloalkanes and arylalkanes have been extensively investigated.[2] In general, the ease of nitration of saturated carbon–hydrogen bonds is tertiary > secondary > primary.[3] Alkyl and cycloalkylbenzenes nitrate preferentially at benzyl positions rather than at other carbon–hydrogen bonds of the substituent or the aromatic nucleus.[3] Nitric

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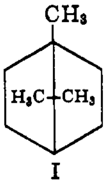
(1) Abstracted in part from the Ph.D. dissertation of D. K. Brain, The Ohio State University, Columbus, Ohio, 1954.

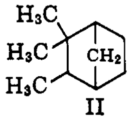
(2) A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, New York, N. Y., 1959, pp. 144–215.

(3) (a) The principal products of nitration of 2,7-dimethyloctane,[3b] ethylbenzene[3c] and cyclohexylbenzene[3d] are 2,7-dimethyl-2-nitroöctane, 1-nitro-1-phenylethane and 1-nitro-1-phenylcyclohexane, respectively; (b) M. I. Konovalov, *Ber.*, **28**, 1855 (1895); (c) M. I. Konovalov, *J. Russ. Phys. Chem. Soc.*, **31**, 255 (1899); (d) N. Kursanoff, *ibid.*, **38**, 1295 (1906).

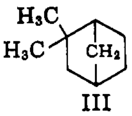
acid reacts with 2,2-dimethylbutane (neohexane) at the secondary neopentyl position to give 2,2-dimethyl-3-nitrobutane[4]; products resulting from carbon-skeleton rearrangement are not obtained. Nitration of camphane (I),[5a] isocamphane (II)[5b] and camphenylane (III)[5c] in the liquid phase only yields secondary nitro compounds; rearrangements of the Wagner–Meerwein type do not occur. Neither I, II nor III are nitrated at the tertiary bridge-head positions; norbornane (IV), however, undergoes bridge-head nitration in the gas phase at 400°.[6]



I



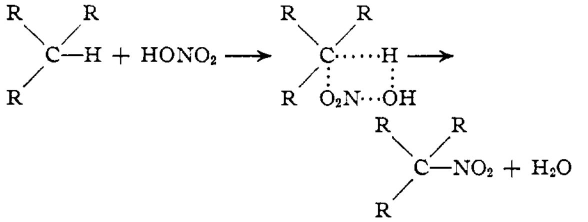
II



III

IV

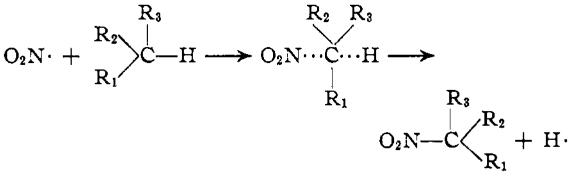
Various mechanisms have been postulated for liquid-phase nitration of saturated hydrocarbons. Ingold[7] has proposed that nitration of an alkane involves electrophilic substitution, SE2, on carbon (eq. 1).



(1)

Hückel and Blohm[8] found that nitration of a mixture of ~ 65% *cis*- and 35% *trans*-decalins, after removal of the secondary nitro compounds, yields an isomeric mixture of 9-nitrodecalins.[8] The tertiary nitro compound obtained as the very major isomer was assumed to be *trans*-9-nitrodecalin.[8] On the basis that the recovered decalins were richer in the *trans* isomer than the initial material, it was proposed that there was nitration of *cis*-decalin to give *trans*-9-nitrodecalin by a Walden inversion process. Nitration of pure *trans*-decalin gave *trans*-9-nitrodecalin. There was no additional interpretation of these experiments and nitration of pure *cis*-decalin was not studied.[8,9]

Stevens and Schiessler[10] have reported that nitration of (−)-3-methyloctane ($\alpha^{25}\mathrm{D}$ −6.5°) with 18% nitric acid at 130° yields (−)-3-methyl-3-nitroöctane ($\alpha^{25}\mathrm{D}$ −0.65°). Although the experimental results did not allow any conclusion with respect to the stereochemistry of displacement and the extent of racemization of the product or the parent hydrocarbon, the optical activity of the product was assumed to eliminate any mechanism involving alkyl radicals ($R_3C\cdot$).[11] It was suggested that nitration occurs by a one-step acceptor–donor inversion mechanism (SR2) in which hydrogen is displaced as an atom and inversion of the asymmetric center is effected (eq. 2). Hass and Riley,[12] reinterpreting these results, propose that liquid-phase nitration involves displacement of hydrogen as a proton rather than as an atom. There was no comment on the stereochemical implications, inversion or retention, of the displacement mechanism suggested.



(2)

More recently Titov[13] suggested that liquid-phase nitration of saturated hydrocarbons with nitric acid or nitrogen dioxide is a radical reaction initiated by attack of nitrogen dioxide on hydrogen (eq. 3). The alkyl radical may then react (in part) with nitrogen dioxide or other nitrating agents to give nitro compounds, nitrites (eq. 4 and 5) and various oxidation products.[13,14]

$$\mathrm{R{-}H} + \cdot\mathrm{NO_2} \longrightarrow \mathrm{R}\cdot + \mathrm{HNO_2} \qquad (3)$$

$$\mathrm{R}\cdot + \cdot\mathrm{NO_2} \longrightarrow \mathrm{R{-}NO_2} \qquad (4)$$

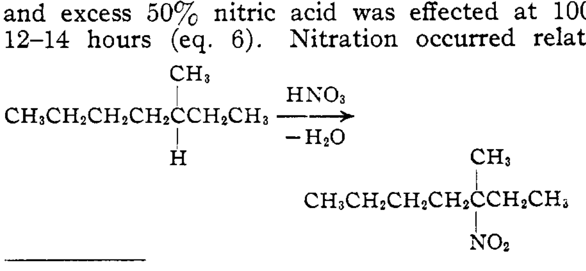
$$\mathrm{R}\cdot + \cdot\mathrm{NO_2} \longrightarrow \mathrm{R{-}ONO} \qquad (5)$$

The mechanism suggested is in agreement with the general ease of nitration of carbon–hydrogen bonds (3° > 2° > 1°)[8,13,15] and observation that the over-all rate of reaction of a hydrocarbon is a function of the concentration of nitrogen dioxide.[13] This mechanism for liquid-phase nitration is similar to that proposed for hydrogen substitution in the vapor-phase reaction.[16]

Upon assessing the facts and the possible mechanisms reported for liquid-phase nitration, it became of interest to study the stereochemistry of nitration in greater detail. An investigation has thus been made of nitration of optically active 3-methylheptane, *cis*- and *trans*-decalins and *cis*- and *trans*-hydrindanes, respectively, with aqueous nitric acid.

Results

Reaction of (+)-3-methylheptane ($[\alpha]^{25}\mathrm{D}$ +9.25°) and excess 50% nitric acid was effected at 100° in 12–14 hours (eq. 6). Nitration occurred relatively


(6)

$$\mathrm{CH_3CH_2CH_2CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{CH_2CH_3} \xrightarrow[-\mathrm{H_2O}]{\mathrm{HNO_3}} \mathrm{CH_3CH_2CH_2CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{CH_2CH_3} \qquad (6)$$

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(4) V. V. Markovnikov, *Ber.*, **33**, 1906 (1900).

(5) (a) S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, **47**, 409 (1915); (b) S. S. Nametkin and L. N. Abakumovskaya, *ibid.*, **47**, 414 (1915); (c) S. S. Nametkin and A. M. Khukhrikova, *ibid.*, **47**, 425 (1915); (d) it is surprising that 2,2,3-trimethyl-3-nitrobicyclo[2.2.1]heptane is not obtained from nitration of II.

(6) (a) H. B. Hass and R. T. Blickenstaff, *J. Am. Chem. Soc.*, **68**, 1431 (1946); (b) G. W. Smith, *ibid.*, **81**, 6319 (1959), has reported that reaction of norbornane with nitrogen dioxide in carbon tetrachloride at 150–200° possibly gives 1-nitronorbornane in low yield.

(7) C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

(8) (a) W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933). (b) The *trans*-9-nitrodecalin was separated from the tertiary mononitration product by crystallization. Reduction of the remaining non-crystalline mixture of isomeric 9-nitrodecalins gave 9-aminodecalins from which *cis*-9-aminodecalin was eventually isolated upon fractional crystallization of its formate salt. (c) The stereochemical assumptions have been shown to be correct by W. G. Dauben, R. C. Tweit and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955). (d) S. Nametkin and O. Madaeff-Ssitcheff, *Ber.*, **59**, 370 (1926), have studied nitration of mixed decalins; the stereochemistries of the nitration products were not determined. (e) Ref. 6b has reported that reaction of commercial decalin with nitrogen dioxide yields 9-nitrodecalin similar in properties to that of the present investigation.

(9) (a) From the previous work,[8a] it could not be determined whether *cis*-decalin was being isomerized by nitric acid. It also could not be concluded that *cis*-decalin undergoes nitration to give *tert*-nitrodecalins more rapidly than does *trans*-decalin. (b) *cis*-Decalin is isomerized to *trans*-decalin by strong acids; N. D. Zelinsky and M. B. Turova-Pollak, *Ber.*, **58**, 1292 (1925).

(10) P. G. Stevens and R. W. Schiessler, *J. Am. Chem. Soc.*, **62**, 2885 (1940).

(11) Such alkyl radicals are expected to lose any initial asymmetry.

(12) H. B. Hass and R. F. Riley, *Chem. Rev.*, **32**, 378 (1943).

(13) A. I. Titov, *J. Gen. Chem. U.S.S.R.*, **16**, 11, 1897 (1946); (b) A. I. Titov, *ibid.*, **18**, 465, 473, 534, 1312 (1948); (c) A. I. Titov, *Usp. khim.*, **21**, 881 (1952); (d) see also ref. 2, pp. 204–209, 258 and 262–266.

(14) (a) Nitrogen dioxide may react with an alkyl radical to give the alkyl nitrite which is subsequently oxidized. Other oxidation reactions of the alkyl radicals may be envisaged which involve nitric oxide, nitric acid or oxygen. (b) Triphenylmethyl radicals react with nitrogen dioxide to give triphenylnitromethane and triphenylmethyl nitrite: W. Schlenk and L. Mair, *Ber.*, **44**, 1170 (1911).

(15) The relative rates of benzylic nitration of the following hydrocarbons are: triphenylmethane > diphenylmethane > toluene.

(16) See G. B. Bachmann and J. P. Chupp, *J. Org. Chem.*, **21**, 655 (1956), and the previous papers by G. B. Bachmann and associates.

rapidly in the hydrocarbon layer as nitrogen dioxide was evolved. The recovered (+)-3-methylheptane ($[\alpha]^{26}\text{D}$ +9.15°) was not appreciably racemized during nitration. The distilled nitration product exhibited pronounced rotation, $[\alpha]^{26}\text{D}$ +7.57°. Since the compounds resulting from attack on any part of the hydrocarbon other than the asymmetric center are optically active regardless of the mechanism of reaction, it was necessary to remove these products from the 3-methyl-3-nitroheptane.

Separation of the isomeric primary and secondary nitro compounds from 3-methyl-3-nitroheptane was based on their conversion to soluble salts by reaction with aqueous or alcoholic bases. The technique involving threefold extraction with 15% aqueous alcoholic (3:1) potassium hydroxide used previously[10] for separating 3-methyl-3-nitroöctane from its isomers was inadequate for removing all of the acidic products from nitration of 3-methylheptane.[17]

It was necessary to treat the nitration product many times in homogeneous solution in methanol with excess sodium methoxide. Negative tests for primary and secondary nitro compounds in the product were finally obtained after a series of drastic treatments.

The resulting 3-methyl-3-nitroheptane, after rectification, exhibited rotations ranging from αD +0.33 to −0.25°; the rotations for the most highly purified sample (l = 2 dm.) upon using very careful techniques at the indicated wave lengths were: −0.07° (6234 λ), −0.08° (5893 λ), −0.11° (5461 λ) and −0.14° (5160 λ). The 3-methyl-3-nitroheptane gave proper analyses; its infrared spectrum revealed weak nitrate, carbonyl and hydroxyl absorptions. The impurities could not be removed by treatment of the limited quantity of product many times with methanolic sodium methoxide, fractional distillation or adsorption chromatography. Concentrated sulfuric acid caused excessive decomposition of the tertiary nitroalkane.

To determine whether the minor contaminants were the source or were obviating any real optical activity of the nitration product, the 3-methyl-3-nitroheptane was hydrogenated catalytically to 3-amino-3-methylheptane. A 30% solution of the amine in absolute ethanol exhibited no rotation at wave lengths from 5160–6234 λ (l = 2 dm.). The reduction product was then converted in 65% yield to N-3-(3-methylheptyl)-N′-phenylthiourea by reaction with phenyl isothiocyanate. Solutions (15% in ethanol) of the crude unrecrystallized derivative (m.p. 74–76°) or the analytically pure derivative (m.p. 79°) exhibited no rotation over the wave length range 5160–6234 λ (l = 2 dm.).[18,19] It is concluded on the basis of the lack of optical rotation of the 3-methyl-3-nitroheptane and its subsequent derivatives that the asymmetry of (+)-3-methylheptane is lost in its conversion to its tertiary nitro derivative. It also appears that the gross stereochemical conclusions from nitration of (−)-3-methyloctane are untenable.[10]

The stereochemistries of nitration of the tertiary hydrogen atoms of *cis*- (99.3%), *trans*- (99.8%) and then mixed (65% *cis*- and 35% *trans*-) decalins, respectively, were investigated. Neither *cis*- nor *trans*-decalins are detectably isomerized by 50% nitric acid at 100° for 5 hours; the refractive indices, infrared spectra and gas-chromatographic properties of each recovered decalin were essentially identical with those of the initial isomer (see Experimental). Pure *cis*-decalin does nitrate more rapidly than does *trans*-decalin. Also, as has been previously reported,[8] in nitration of a mixture of 65% *cis*- and 35% *trans*-decalins, the recovered hydrocarbon contained a higher percentage of *trans*-decalin than did the initial mixture. It cannot be concluded yet, however, that *cis*-decalin undergoes nitration at tertiary positions faster than does *trans*-decalin (as is probably the case) since the over-all reactivities of *cis*- and *trans*-decalins result from nitration of secondary and tertiary hydrogen atoms.

The tertiary nitrodecalins from *cis*-, *trans*- and mixed decalins, respectively, were separated from their secondary nitro isomers and purified by prolonged treatment with methanolic sodium methoxide. The alkaline extractions were continued until the insoluble nitration product no longer gave a positive pseudonitrole test for secondary nitro compounds. Upon distillation of each reaction product, 9-nitrodecalin was obtained of near identical properties; the physical constants of the 9-nitrodecalin (see Experimental, Table I) are similar to those previously reported.[8a,d]

Each of the three nitration products was reduced with hydrogen and Raney nickel to 9-aminodecalin in ~95% yield (Table I). The physical properties of the samples of 9-aminodecalin were almost identical and agreed satisfactorily with those previously reported.[8a,d] Acetylation of each 9-aminodecalin gave pure *trans*-N-9-decalylacetamide, m.p. 183°[8]; the over-all yields for conversion of each 9-nitrodecalin to the pure solid derivative ranged at minimum from 77 to 86.5% (Table II). The stereochemistry of the *trans*-N-9-decalylacetamide was confirmed upon comparison with authentic material.[20] It may thus be concluded that nitration of *cis*-, *trans*- or mixed decalins yields identical 9-nitrodecalin; stereochemical analysis of the nitration product based on the yields of its conversion to *trans*-N-9-decalylacetamide reveal that it is principally (at least 77–86.5%) *trans*-9-nitrodecalin.

The nitration products from *cis*-, *trans*- and mixed decalins contain *trans*-9,10-dinitrodecalin (m.p. 169°; mixed melting points of the samples were not depressed). The stereochemistry of *trans*-9,10-dinitrodecalin was assigned on the basis of the differences in properties of its reduction product, *trans*-9,10-diaminodecalin, and the *cis*-9,10-diaminodecalin obtained from reaction of *cis*-decalin-9,10-dicarboxylic acid with hydrazoic acid.[21] The isolation of *trans*-9,10-dinitrodecalin from nitration of either *cis*- or *trans*-decalins is consistent with the observation that the stereochemistry of substitution of nitro groups for tertiary hydrogen atoms is independent of the stereochemistry of the initial decalin; the *trans*-9,10-dinitrodecalin is presumed to have been derived primarily from nitration of *trans*-9-nitrodecalin.

Nitration of 99.9% *cis*- and 99.3% *trans*-hydrindanes, respectively, in the liquid phase was studied to obtain information concerning the stereochemistries of substitution at the tertiary positions to give 8-nitrohydrindanes. In general, the procedures for nitration and the methods for relating the structures of the 8-nitrohydrindane are similar to those used in nitration of the decalins. The *cis*- and *trans*-hydrindanes recovered from the nitration experiments were identical with the

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(17) The method suffers from the lack of solubility of the nitro compounds in the solvent system.

(18) Attachment of a large polarizable group to such an asymmetric center usually results in exhanced rotation. F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 456 (1944), have found that the rotation of (+)-2-aminooctane ($[\alpha]^{17}\text{D}$ −8.53°) is greatly increased upon conversion to its N-benzoyl derivative ($[\alpha]^{17}\text{D}$ −62.1°, $[\alpha]^{17}{}_{4358}$ −125°).

(19) The physical constants of the products derived from nitration of (±)-3-methylheptane, subsequent reduction and conversion to the corresponding thiourea correspond almost identically with those from (+)-3-methylheptane.

(20) Generously provided by Dr. W. G. Dauben, Chemistry Department, University of California, Berkeley, Cal.

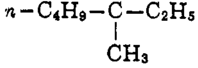
(21) These experiments by J. G. Gardikes, Ph.D. thesis, The Ohio State University, Columbus, Ohio, 1960, are to be published as part of a separate communication; (b) Schmidt reactions of carboxylic acids occur with retention of stereochemistry.

initial pure hydrocarbons; *cis*-hydrindane nitrates more rapidly than does *trans*-hydrindane.[22]

The physical properties and the infrared spectra of the 8-nitrohydrindane[23] obtained from *cis*- and *trans*-hydrindanes, respectively, were essentially identical (see Experimental). The samples of 8-nitrohydrindane were related upon their near-quantitative hydrogenation to practically identical 8-aminohydrindane and subsequent conversion to identical N-8-hydrindylacetamide.[24] The over-all yield for conversion of the 8-nitrohydrindane from *cis*-hydrindane to pure N-8-hydrindylacetamide was at least 83%, that from *trans*-hydrindane was greater than 73%. The similarity of the 8-aminohydrindane derived from *cis*- and *trans*-hydrindanes was further demonstrated upon their conversion to identical N-8-hydrindylbenzamide in excellent yields. The stereochemistry[25] and the absolute isomer composition of the 8-nitrohydrindane obtained has as yet not been determined. For the purposes of the present investigation it is satisfactory to conclude that nitration of *cis*- and *trans*-hydrindanes yields identical 8-nitrohydrindane and thus the structure of the tertiary nitration product is independent of the initial hydrindane.

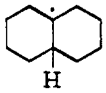
Discussion

From the stereochemistries of nitration of the tertiary hydrogens of (+)-3-methylheptane, *cis*- and *trans*-decalins and *cis*- and *trans*-hydrindanes, it is apparent that all mechanisms of a bimolecular type are excluded in which a nitro group is substituted directly on a hydrocarbon. The substitution reactions must take place through one or more of three paths involving formation of carbonium ions, carbanions or free radicals. The mechanism as proposed by Titov[13] in which nitrogen dioxide (or an analogous reagent) extracts a hydrogen atom from a hydrocarbon to give the hydrocarbon radical is in best agreement with the experimental data now available. Possible conversion of (+)-3-methylheptane to the 3-methyl-3-heptyl radical results in an intermediate which may lose its asymmetry and then be converted to racemic 3-methyl-3-nitroheptane. Both *cis*- and *trans*-decalins yield the 9-decalyl radical VI upon loss of tertiary hydrogen; subsequent reaction of intermediate radical VI to give *trans*-9-nitrodecalin more rapidly than the *cis*-nitro isomer is relatable to steric factors.[26,27] Similar interpretations are applicable to the conversion of 9-nitrodecalins to *trans*-9,10-dinitrodecalin and of *cis*- and *trans*-hydrindanes *via* intermediate VII to identical 8-nitrohydrindane.[27]

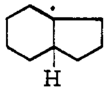


$$n\text{-}C_4H_9-\overset{\bullet}{\underset{\substack{|\\ CH_3}}{C}}-C_2H_5$$

V



VI



VII

A reaction mechanism involving hydrocarbon radicals is also consistent with the observations that: (1) benzylic and tertiary hydrogens are nitrated more rapidly than are secondary or primary, (2) carbon-skeleton rearrangement does not occur during nitration of neopentyl derivatives or of appropriate bicyclo[2.2.1]heptanes (I–III), (3) substitution of tertiary bridge-head hydrogen of bicyclo[2.2.1]heptanes does not occur except at relatively high temperatures, (4) the rate of nitration of a hydrocarbon in an inert solvent is related to the concentration of nitrogen dioxide and (5) nitration of a hydrocarbon by nitric acid is not accelerated by strong acids or greatly affected by solvents of different dielectric strengths.

Experimental

Mixed decalin (*ca.* 65% *cis*- and 35% *trans*-), b.p. 81–83° (20 mm.), $n^{25}\mathrm{D}$ 1.4751; *cis*-decalin, 99.3% purity,[28a,b] b.p. 195.7°, $n^{25}\mathrm{D}$ 1.4790; *trans*-decalin, 99.8% purity,[28a,b] b.p. 187.25°, $n^{25}\mathrm{D}$ 1.4671; *cis*-hydrindane, 99.9% purity,[28a] b.p. 167.8°, $n^{20}\mathrm{D}$ 1.4720; and *trans*-hydrindane, 99.3% purity,[28a] b.p. 161.0°, $n^{20}\mathrm{D}$ 1.4636, were the gifts of the American Petroleum Institute, Project 31, Columbus, Ohio.

Optically-active 3-methylheptane was prepared from (−)-2-ethylhexanoic acid (method 1) and from (−)-2-methyl-1-butanol (method 2); the two routes are described in so far as they involve new methods or procedures, advantageous techniques or improved optical values and yields. (−)-2-Methyl-1-butanol ($[\alpha]^{25}\mathrm{D}$ −5.76°, optical purity *ca.* 97.5%, b.p. 129°, $n^{20}\mathrm{D}$ 1.4107; lit.[29] $[\alpha]^{20}\mathrm{D}$ −5.90° (optically pure), b.p. 129° (760 mm.)) was obtained from Dr. T. Burton, Utah State University, Logan, Utah, from the Dow Chemical Co., and by rectification of fermentation amyl alcohol (United States Industrial Chemicals Co.). For synthesis of large quantities of (+)-3-methylheptane, method 2 is preferred.

Method 1. (−)-2-Ethyl-1-hexanol.—(+)-2-Ethylhexanoic acid upon resolution with quinine in 40% acetone (6 recrystallizations) and steam distillation from dilute hydrochloric acid gave (−)-2-ethylhexanoic acid (40% yield of the possible (−)-acid); $[\alpha]^{30}\mathrm{D}$ −8.30°, b.p. 83° (1 mm.), $n^{25}\mathrm{D}$ 1.4231; lit. $[\alpha]^{31}\mathrm{D}$ +8.89°,[30a] b.p. 120° (13 mm.), $n^{25}\mathrm{D}$ 1.4229.[30b] (−)-2-Ethylhexanoic acid ($[\alpha]^{30}\mathrm{D}$ −7.60°) was converted by azeotropic distillation with excess ethanol, benzene and catalytic amounts of sulfuric acid to (−)-ethyl 2-ethylhexanoate (96% yield), $[\alpha]^{28}\mathrm{D}$ −6.04°, b.p. 87–88° (20 mm.), $n^{25}\mathrm{D}$ 1.4128; lit. [30a]$[\alpha]^{17}\mathrm{D}$ −6.79° (from 2-ethylhexanoic acid of $[\alpha]^{16}\mathrm{D}$ −8.75°), b.p. 96–97° (35 mm.), $n^{13}\mathrm{D}$ 1.4185.

Procedure 1.—(−)-2-Ethylhexanoic acid (46.0 g., 0.32 mole, $[\alpha]^{30}\mathrm{D}$ −8.50°) in ethyl ether (100 ml.) was added dropwise to lithium aluminum hydride (25.2 g., 0.66 mole) in ethyl ether (250 ml.) at 0–5°. Water and 10% sulfuric acid were added after 0.5 hour. Upon isolation by conventional techniques, (−)-2-ethyl-1-hexanol (37.15 g., 0.286 mole) was obtained in 90% yield, $[\alpha]^{19.3}\mathrm{D}$ −3.44°, b.p. 91–93° (20 mm.), $n^{25}\mathrm{D}$ 1.4286; lit.[30a] $[\alpha]^{30}\mathrm{D}$ +4.03° (from (+)-2-ethylhexanoic acid, $[\alpha]^{31}\mathrm{D}$ +8.89°, and thence (+)-ethyl 2-ethylhexanoate and subsequent reduction with sodium in acetic acid[30a]), b.p. 92–94° (22 mm.), $n^{17}\mathrm{D}$ 1.4325.[30a]

Procedure 2.—(−)-Ethyl 2-ethylhexanoate (49.2 g., 0.286 mole, $[\alpha]^{28}\mathrm{D}$ −6.04°) in ethyl ether (75 ml.) was added to stirred lithium aluminum hydride (80 g., 0.209 mole) in ethyl ether (125 ml.) at 5–10°. After 0.5 hour, water and 10% sulfuric acid were added, and (−)-2-ethyl-1-hexanol (34.25 g., 0.263 mole, 92% yield) was obtained, $[\alpha]^{30.2}\mathrm{D}$ −3.05°, b.p. 90° (18 mm.), $n^{25}\mathrm{D}$ 1.4290.

(−)-3-Methylheptane.—(−)-2-Ethyl-1-hexanol ($[\alpha]^{1.93}\mathrm{D}$ −3.44°) was converted to (−)-1-bromo-2-ethylhexane (64% yield) by reaction with phosphorus tribromide; $[\alpha]^{27}\mathrm{D}$ −5.34°, b.p. 106.5–108° (54 mm.), $n^{25}\mathrm{D}$ 1.4516; lit.[30b] $[\alpha]^{25}\mathrm{D}$ −2.59° (from (−)-2-ethyl-1-hexanol of $[\alpha]^{25}\mathrm{D}$ −1.53°), b.p. 110–118° (71 mm.), $n^{25}\mathrm{D}$ 1.4526. A solution of the (−)-1-bromo-2-ethylhexane (32.30 g., 0.167 mole) in tetrahydrofuran (50 ml.) was added to a refluxing mixture of lithium aluminum hydride (7.6 g., 0.20 mole) and tetrahydrofuran (100 ml.). After 1 hour the mixture was cooled, and water–tetrahydrofuran (50 ml., 40:60 by volume) and then 10% sulfuric acid (300 ml.) were added. Isolation of the product and subsequent rectification gave (−)-3-methylheptane (17.3 g., 0.151 mole, 90% yield), $[\alpha]^{21.8}\mathrm{D}$ −7.93°, b.p. 117–117.2°, $n^{25}\mathrm{D}$ 1.3971; lit. $[\alpha]^{18}\mathrm{D}$ +6.70°[30a] (from (+)-2-ethyl-1-hexanol, $[\alpha]^{30}\mathrm{D}$ +4.03°, and thence 2-ethyl-1-iodohexane, and subsequent reduction with zinc and acetic acid), b.p. 118.9° (760 mm.),[28a] $n^{20}\mathrm{D}$ 1.3985.[28a]

Method 2. (+)-5-Methyl-1-heptene.—(−)-2-Methyl-1-butanol ($[\alpha]^{20}\mathrm{D}$ −5.76°) was converted to (+)-1-bromo-2-methyl-

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[22] As with the decalins, because of the competing reactions, it cannot yet be concluded that nitration of the tertiary positions of *cis*-hydrindane occurs more rapidly than that of *trans*-hydrindane.

[23] Each nitration product was treated with methanolic sodium methoxide until it did not give a test for secondary nitro compounds; distillation gave material of analytical purity.

[24] The individual solid derivatives were analytically pure and spectroscopically similar; their melting points were not depressed on admixture.

[25] Synthesis of *cis*-N-8-hydrindylacetamide and *cis*-N-8-hydrindylbenzamide is to be investigated.

[26] The present interpretation is based on the assumption that *cis*-9-nitrodecalin, if formed in appreciable quantities, is not isomerized by nitric acid to *trans*-9-nitrodecalin. Such an assumption appears reasonable since *cis*-decalin is not isomerized to its *trans* isomer by hot 50% nitric acid.

[27] These interpretations are also based on kinetic rather than thermodynamic control.

[28] (a) American Petroleum Institute Cumulative Report, 1959; (b) W. F. Seyer and R. D. Walker, *J. Am. Chem. Soc.*, **60**, 2125 (1938).

[29] W. F. Barrow and R. G. Atkinson, *J. Chem. Soc.*, 638 (1939).

[30] (a) J. Kenyon and B. C. Platt, *ibid.*, 635 (1939); (b) P. A. Levene, A. Rothen and G. M. Meyer, *J. Biol. Chem.*, **115**, 411 (1936).

butane (89% yield) by reaction with phosphorus tribromide[31a,b]; the bromide was extracted with concd. sulfuric acid at −10°, water, 10% sodium bicarbonate, and saturated sodium chloride $[\alpha]^{24.3}_{\text{D}}$ +4.04°, n^{25}_{D} 1.4430; lit. $[\alpha]^{25}_{\text{D}}$ +4.05°,[31b] n^{20}_{D} 1.4450.[32] The undistilled bromide was stored over anhydrous potassium carbonate at 0–5°.

Procedure 1.—Reaction of allyl bromide (10 g.) in ethyl ether (10 ml.) with powdered magnesium (382 g., 15.9 g.-atoms) was initiated. After diluting the stirred mixture with anhydrous ethyl ether (2.5 liters), allyl bromide (632 g., a total of 5.3 moles) was added at a rate such as to allow gentle reflux. The mixture was stirred at 25–30° for 6 hours and then refluxed for 1 hour. After filtering the excess magnesium, the yield of Grignard reagent (4.50 moles, 85%) was determined by hydrolyzing an aliquot (the yields of Grignard reagent ranged from 85–100% for numerous experiments; *ca.* 10% excess of Grignard reagent over 1-bromo-2-methylbutane was used in every reaction).

(+)-1-Bromo-2-methylbutane (623 g., 4.13 moles, $[\alpha]^{25}_{\text{D}}$ +4.00°) was added to the Grignard reagent in 30 minutes. After the mixture had been refluxed for 2 weeks, it was hydrolyzed at 0° with 30% sulfuric acid (450 ml.) to give, after separation and initial purification, crude (+)-5-methyl-1-heptene (448 g., 4.0 moles) in 97% yield, b.p. 110–114°. Since the product gave a strong test for an organic bromide, it was stirred at 25° with saturated aqueous silver nitrate (250 ml.) for 50 hours. After the silver bromide had been filtered and washed with ether, the organic material was combined, washed with water and saturated sodium chloride, dried over calcium chloride, and then rectified to give (+)-5-methyl-1-heptene (380 g., 3.39 moles, 83% yield), $[\alpha]^{25}_{\text{D}}$ +9.37°. b.p. 112°, n^{25}_{D} 1.4088; lit.[33] $[\alpha]^{26}_{\text{D}}$ +10.20°, b.p. 113°, n^{25}_{D} 1.4076.[33] The final yields of pure olefin ranged from 70–85% for the various experiments that were conducted.

Procedure 2.—(+)-1-Bromo-2-methylbutane ($[\alpha]^{25}_{\text{D}}$ + 4.00°, 75 g., 0.55 mole) in ethyl ether (330 ml.) was dropped slowly on powdered magnesium (27 g., 1.1 g.-atoms), and the mixture was stirred for 1 hour and then filtered. Allyl bromide (80 g., 0.66 mole) in ethyl ether (80 ml.) was added in 30 minutes, and the mixture was refluxed for 20 hours. The product was worked up as in procedure 1 to give (+)-5-methyl-1-heptene[33] (30.85 g., 0.275 mole) in 50% yield, $[\alpha]^{25}_{\text{D}}$ +8.50°, b.p. 110–112°, n^{25}_{D} 1.4058.

Under the conditions described, procedure 1 was more effective than procedure 2 and thus was usually used for preparing (+)-5-methyl-1-heptene.

(+)-3-Methylheptane.—(+)-5-Methyl-1-heptene ($[\alpha]^{25}_{\text{D}}$ +9.37°, 78.0 g., 0.696 mole) in ethyl ether (150 ml.) was hydrogenated (50 p.s.i.) to give, after filtration and rectification, (+)-3-methylheptane (73.4 g., 0.644 mole, 92% yield), $[\alpha]^{26}_{\text{D}}$ +9.25°, b.p. 117°, n^{20}_{D} 1.3995; lit.[31b] $[\alpha]^{26}_{\text{D}}$ +9.34°, n^{25}_{D} 1.3962. Methanol and glacial acetic acid were also used as solvents for reduction; ethyl ether, however, is the most practical since methanol forms an azeotrope with 3-methylheptane, and acetic acid must be extracted from the reaction product.

Nitration of (+)-3-Methylheptane.—(+)-3-Methylheptane ($[\alpha]^{26}_{\text{D}}$ +9.25°, 228 g., 2.0 moles) was heated to 95° with 50% nitric acid (12 moles of HNO_3). An exothermic reaction ensued, and large quantities of nitrogen dioxide were evolved. After the heterogeneous mixture had been heated at 100° for 12 hours, the organic layer was removed; the aqueous layer was extracted with ethyl ether. The organic products were combined, washed with water, 20% aqueous sodium bicarbonate, and saturated sodium chloride solution and then dried. Rectification gave: (1) (+)-3-methylheptane (101 g., 44% recovery), $[\alpha]^{26}_{\text{D}}$ +9.15°, b.p. 45–51° (57 mm.), n^{25}_{D} 1.3987; (2) crude nitroöctanes (36.6 g.), $[\alpha]^{26}_{\text{D}}$ +9.83° to +7.57°, b.p. 70–90° (8 mm.), n^{25}_{D} 1.4320–1.4384; (3) crude mono- and polynitroalkanes (11.46 g.), b.p. 73–83° (1 mm.), n^{25}_{D} 1.4450: and (4) residue (52.6 g.), n^{25}_{D} 1.4633. On the basis of physical constants and infrared spectra, the recovered (+)-3-methylheptane is practically identical with the initial hydrocarbon.

Fractions 2 and 3 were dissolved in 3 *N* sodium methoxide (*ca.* 1.5 moles of base/mole of nitroöctane) in methanol and stirred for 2 days. The alkaline solution was diluted with water and extracted with ethyl ether; the ether extracts were washed with brine and dried over Drierite. The recovered nitroalkane was distilled and examined polarimetrically (after the product had been treated twice with methanolic sodium methoxide, the nitrooctane exhibited uncorrected rotations of $[\alpha]^{25}_{\text{D}}$ +0.21° to −0.45°). After four treatments with sodium methoxide, there was no evidence for base-soluble material in the product, and negative tests[34] for primary and secondary nitro compounds were obtained. The product was rectified to give the following water-white fractions: (1) 2.11 g., b.p. 72–81° (10 mm.), n^{20}_{D} 1.4324; (2) 3-methyl-3-nitroheptane (1.95 g.), b.p. 81–82° (10 mm.), n^{25}_{D} 1.4330, d^{25}_{4} 0.936; (3) impure 3-methyl-3-nitroheptane (0.75 g.), b.p. 82–83° (10 mm.), n^{25}_{D} 1.4336; and (4) residue.

Anal.[35] Calcd. for $C_8H_{17}NO_2$: C, 60.38; H, 10.69; N, 8.80. Found: C, 60.49; H, 10.73; N, 8.81.

The corrected optical rotations of the 3-methyl-3-nitroheptane at the following wave lengths were: −0.04°, 6234 λ; −0.05°, 5893 λ; −0.06°, 5461 λ; −0.07°, 5160 λ.[36] The infrared spectrum of this product exhibits strong absorption for an aliphatic nitro group (6.47 and 7.40 μ)[35b]; minor absorption indicated that nitrato (6.10 μ),[35c] hydroxy and carbonyl compounds were present.[35a,c,37] Attempts to purify (distillation, chromatography, treatment with concd. or dil. sulfuric acid) the 3-methyl-3-nitroheptane further resulted in serious losses of product. The product was thus reduced to 3-amino-3-methylheptane and then converted to N-phenyl-N′-3-(3-methylheptyl)-thiourea; the optical rotations of the amine and its solid derivative were then determined.

Reduction of 3-Methyl-3-nitroheptane from (+)-3-Methylheptane; (±)-N-Phenyl-N′-3-(3-methylheptyl)-thiourea.—3-Methyl-3-nitroheptane ($[\alpha]^{26}_{\text{D}}$ −0.04°, 5.71 g., 0.0359 mole) was hydrogenated (50 p.s.i.) over Raney nickel in ethyl ether (40 ml.). Distillation of the filtered product gave colorless, crude 3-amino-3-methylheptane, 1.36 g., b.p. 63–65° (27 mm.), n^{25}_{D} 1.4212–1.4223.[38] The infrared spectrum of the 3-amino-3-methylheptane gave characteristic absorption for N–H bonds and there was no absorption for a nitro group.[35] A 30% solution of the amine (0.64 g. in 1.50 g. of ethanol; 2 dm.) exhibited no rotation at 6234, 5893, 5461 and 5160 λ, respectively.

The 3-amino-3-methylheptane (0.5 g., 0.0039 mole) was heated with phenyl isothiocyanate (0.55 g., 0.004 mole) for 3 minutes. The colorless oil solidified after 12 hours at 5°. The white solid was crushed and washed with a few drops of ligroin. The crude derivative (0.64 g., 0.026 mole, 67% crude yield, m.p. 74–76°) in absolute ethanol (3.56 g., a 15.3% solution) gave no detectable rotation in a 2-dm. tube at 6234, 5893, 5461 and 5160 λ, respectively.

The N-phenyl-N′-3-(3-methylheptyl)-thiourea, upon recrystallization from 40% aqueous ethanol (58% yield), melted at 79° and exhibited no rotation. There was no depression in melting point of this product upon admixture with the derivative (m.p. 79°) derived from the sequence involving (±)-3-methylheptane.

Anal. Calcd. for $C_{14}H_{24}N_2S$: C, 68.17; H, 9.09; N, 10.62. Found: C, 68.24; H, 9.06; N, 10.56.

Nitration of *cis*-, *trans*- and Mixed Decalins.—Liquid-phase nitrations of *cis*-, *trans*- and mixed decalins, respectively, were effected essentially under identical conditions. The procedure used with *cis*-decalin is described; the results obtained with *trans*- and commercial decalins are summarized.

cis-Decalin (71.4 g., 0.517 mole, n^{25}_{D} 1.4808, infrared absorption[39] for the *cis* structure at 11.72 and 12.00 μ) was refluxed for 3 hours with 50% nitric acid (3 moles of HNO_3). The aqueous layer was extracted with ethyl ether. The extracts and the nitrodecalin layer were combined, neutralized, dried over Drierite, and concentrated. Distillation of the residue gave: (1) *cis*-decalin (22.5 g., 32% recovery), b.p. 38–41° (2 mm.), n^{25}_{D} 1.4801; (2) crude nitrodecalins (15.19 g.), b.p. 79–125° (2 mm.), n^{25}_{D} 1.4923–1.5008; and (3) residue (20.1 g.), higher boiling. The infrared absorption, the refractive index[39] and the gas-chromatographic analysis of the recovered decalin indicate that it is identical with the initial *cis*-decalin.

The crude nitrodecalins were combined with similar products from three other nitrations and treated with methanolic sodium methoxide (4 times) until a negative test for secondary nitro groups was obtained.[34] Thus from reaction of 1.49 moles of decalin there was obtained 22.5 g. (0.123 mole) of crude 9-nitrodecalin (8.3% conversion). Rectification of the product gave, after removal of the forerun: (1) 3.9 g., b.p. 81–85° (1 mm.), n^{25}_{D} 1.4920; (2) 9-nitrodecalin (analyzed), 10.1 g., b.p. 85–86° (1

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[31] (a) J. D. Bartleson, R. E. Burk and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946); (b) R. L. Burwell and G. S. Gordon, *ibid.*, **70**, 3128 (1948).

[32] F. C. Whitmore and J. H. Olewine, *ibid.*, **60**, 2569 (1938).

[33] S. F. Velick and J. English, *J. Biol. Chem.*, **160**, 473 (1945).

[34] Reference 12, p. 378.

[35] (a) The product analyzed was (±)-3-methyl-3-nitroheptane obtained by nitration of (±)-3-methylheptane; b.p. 82° (10 mm.), n^{20}_{D} 1.4339, d^{25}_{4} 0.9280; *MR*D (calcd.) 44.84; *MR*D (found) 44.37. This product exhibited major absorption (uncorrected) for a nitro group[35b] (6.48 and 7.42 μ) and minor absorption for hydroxyl, carbonyl and nitrate[35c] (6.10 μ) groups. (b) J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955). (c) It is very difficult to remove the contaminants in the nitration product; see subsequent experimental.

[36] The rotations reported were obtained in a properly-positioned precision-calibrated polarimeter corrected against blank samples.

[37] The 3-methyl-3-nitroheptane from seven experiments similar to that described exhibited minor absorption for carbonyl, hydroxyl and nitrate groups and had the following physical constants: $[\alpha]^{20}_{\text{D}}$ 0.23 to −0.28° (uncorrected), b.p. 78–81° (10 mm.) and n^{25}_{D} 1.4321–1.4373.[35a]

[38] (±)-3-Amino-3-methylheptane from (±)-3-methyl-3-nitroheptane (60% yield) as derived from (±)-3-methylheptane had physical constants (b.p. 63–65° (28 mm.) and n^{25}_{D} 1.4223) and an infrared spectrum almost identical with that of (±)-3-amino-3-methylheptane from (+)-3-methylheptane.

[39] J. Seidman, *Anal. Chem.*, **23**, 559 (1951).

TABLE I

PROPERTIES OF 9-NITRODECALIN OBTAINED FROM NITRATION OF DECALIN

	9-Nitrodecalin				
Parent decalin	B.p., °C.	mm.	$n^{25}{}_{\mathrm{D}}$	$d^{25}{}_{4}$	Infrared absorption,[a] μ
cis-[b]	85–86	1	1.4933	1.084	C–H: 3.38, 6.90, 7.25
trans-[b]	79–81	0.8	1.4919	1.082	C–NO_2: 6.50, 7.40
trans-[c]	122–125	18	$n^{25.4}{}_{\mathrm{He}}$ 1.4922	1.083	
Mixed[b,d]	87–88	1.3	1.4925	1.081	Unassigned[f]: 10.70, 11.90, 12.10
Mixed[e]	96–97	2	1.4924	1.0847	

[a] Routine determinations (uncorrected). [b] From the present nitration experiments. [c] Lit., ref. 8a. [d] Approximately 65% *cis*- and 35% *trans*-decalins. [e] Lit., ref. 8d. [f] Possibly due to the *trans*-ring system.

mm.) $n^{25}{}_{\mathrm{D}}$ 1.4933, $d^{25}{}_{4}$ 1.084, *MR*D (calcd.) 49.80, *MR*D (found) 49.09; (3) crude 9-nitrodecalin, 2.5 g., b.p. 86–90° (1 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4941; and (4) residue. The 9-nitrodecalin (fraction 2) gave strong absorption for nitro[35b] (6.50 and 7.40 μ) and minor absorption for nitrate[35b] (6.10 μ) groups[40]; its physical properties and infrared absorption were almost identical with the 9-nitrodecalin obtained from mixed and *trans*-decalins, respectively, and with that previously reported (Table I).

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.55; H, 9.29; N, 7.65. Found: C, 65.73; H, 9.22; N, 7.49.

Nitration of *trans*-decalin ($n^{25}{}_{\mathrm{D}}$ 1.4671; infrared absorption for the *trans* structure at 10.82, 11.90 and 12.20 μ) resulted in 51% recovery of *trans*-decalin (b.p. 65° (12 mm.)); the boiling point, refractive index ($n^{25}{}_{\mathrm{D}}$ 1.4672) and infrared absorption of the recovered decalin were identical with that of the initial *trans*-decalin. A total of 27.4 g. (0.15 mole) of crude 9-nitrodecalin was obtained from nitration of 1.26 moles of *trans*-decalin (12% conversion). The distilled 9-nitrodecalin (*MR*D (calcd.) 49.80, *MR*D (found) 49.66) was practically identical (Table I) with that obtained from *cis*-decalin. The product also exhibited weak absorption for nitrite (5.80 μ) and nitrate (6.10 μ) groups.[35b]

Nitration of mixed decalin ($n^{25}{}_{\mathrm{D}}$ 1.4751; absorption[39] for *trans*-decalin, 10.81, 11.92, and 12.12 μ[39]; for *cis*-decalin, 11.72 and 12.00 μ) as described previously resulted in 50% recovery of the decalin ($n^{25}{}_{\mathrm{D}}$ 1.4723) and in formation of 9-nitrodecalin (Table I) similar in properties to that obtained in the previous experiments. The refractive index and the infrared spectrum of the recovered decalin indicated that it is richer in the *trans* isomer than is the parent.

Proof of Structure of 9-Nitrodecalin; *trans*-9-Decalylamine and *trans*-N-9-Decalylacetamide.—The 9-nitrodecalin (Table I) obtained from nitration of *cis*-, *trans*- and mixed decalins, respectively, was converted individually to 9-decalylamine and to N-9-decalylacetamide in order to determine the similarity, the homogeneity and the stereochemistry of each tertiary nitration product. The conversions of the samples of 9-nitrodecalin to 9-decalylamine and then to N-9-decalylacetamide are summarized in Table II. The technique for converting 9-nitrodecalin derived from *cis*-decalin to N-9-decalylacetamide is described.

9-Nitrodecalin (5.0 g., 0.0274 mole) in 95% ethanol (50 ml.) was hydrogenated (50 p.s.i.) over Raney nickel for 3 hours. After the catalyst and the ethanol had been removed, 9-decalylamine (Table II, 4.05 g., 0.0266 mole, 97% yield) remained. The yield, refractive index and infrared spectra of the undistilled 9-decalylamine[41] (there was no absorption for a nitro group[35b]) were almost identical with that obtained from 9-nitrodecalin derived from *trans*- and from mixed decalins; the physical constants of the undistilled 9-decalylamine agree satisfactorily with those previously reported (Table II).

The 9-decalylamine (1.95-g. aliquot, 0.0127 mole) was shaken with excess acetic anhydride and 20% sodium hydroxide (3 ml.). The precipitate that formed was crushed, washed with water and dried to give crude N-9-decalylacetamide (2.36 g., 0.0121 mole, 95% crude yield from 9-decalylamine), m.p. 171–176°. Recrystallization of the product gave (at minimum) 2.1 g. of pure *trans*-N-9-decalylacetamide, m.p. 183°; the composition of the initial derivative is thus at least 89% *trans*-N-9-decalylacetamide (Table II). The melting point of the derivative was not depressed upon addition of N-9-decalylacetamide derived from *trans*- or mixed decalins or by authentic *trans*-N-9-decalylacetamide, m.p. 183°. Nitration of *trans*- and *cis*-decalins yields 9-nitrodecalin which is at minimum 80.0 and 89.3% the *trans* derivative (Table II). Reduction of *trans*-9-nitrodecalin thus yields *trans*-9-decalylamine; acetylation of *trans*-9-decalylamine then gives *trans*-N-9-decalylacetamide.

TABLE II

CONVERSION OF 9-NITRODECALIN TO 9-DECALYLAMINE AND TO N-9-DECALYLACETAMIDE

	9-Decalylamine		*trans*-N-9-Decalylacetamide		
Parent decalin[a]	Yield, %[b]	$n^{25}{}_{\mathrm{D}}$	Yield, %[c]	Min. % of initial derivative[d]	M.p., °C.[e]
cis-	97	1.4922	86.5	89.0	183
trans-	98	1.4927	77.0	80.0	183
trans-[f]	. .	1.4921[g]			183
Mixed	95	1.4923	85.0	89.3	183
Mixed[f]	. .	1.4932[g]			

[a] Hydrocarbon nitrated to give 9-nitrodecalin of properties summarized in Table I. [b] Yield (max.) of undistilled 9-decalylamine from hydrogenation of 9-nitrodecalin. [c] Over-all yield (min.) of pure *trans*-N-9-decalylacetamide, m.p. 183°, from 9-nitrodecalin. [d] The minimum percentage of pure *trans*-N-9-decalylacetamide in the crude initial product isolated from reaction of 9-decalylamine and acetic anhydride. [e] Lit.,[8a] m.p. 183°. [f] Ref. 8a, see Table I. [g] Distilled.

***trans*-9,10-Dinitrodecalin.**—*trans*-9,10-Dinitrodecalin was isolated upon crystallization of the distillation residues of the base-insoluble products from nitration of either *cis*-, *trans*- or mixed decalins. Recrystallization of the solid product from ethyl ether gave large, clear rhombic crystals, m.p. 169°, lit.[8a] m.p. 169°. The melting point of the 9,10-dinitrodecalin obtained from nitration of each decalin was undepressed upon admixture with authentic *trans*-9,10-dinitrodecalin.[21a] *trans*-9,10-Dinitrodecalin is similar to *trans*-decalin and *trans*-9-nitrodecalin[40] in that it exhibited infrared absorption at 10.62, 11.80 and 12.15 μ, respectively (Table I).

Nitration of *cis*- and *trans*-Hydrindanes.—*cis*-Hydrindane[42] (99.9%, 124 g., 1.0 mole, $n^{25}{}_{\mathrm{D}}$ 1.4700) was refluxed for 5 hours with 50% nitric acid (6 moles of HNO_3). The reaction mixture was handled as described in nitration of *cis*-decalin and then distilled to give: (1) *cis*-hydrindane (34.0 g., 28% recovery), b.p. 62° (20 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4697; and (2) crude nitrohydrindanes (17.5 g.), b.p. 93–120° (1 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4953. The recovered hydrindane was essentially unchanged from the initial *cis*-hydrindane since their physical properties and infrared spectra[42] were practically identical.

The nitration product was combined with the nitrohydrindanes from two similar experiments and extracted with 3 *N* sodium methoxide in methanol until all secondary nitro compounds had been removed. From reaction of 1.80 moles of hydrindane there was obtained 21.4 g. of colorless and base-insoluble nitrated hydrindane. Rectification gave 8-nitrohydrindane in the following fractions: (1) 3.00 g., b.p. 66–68° (0.8 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4876; (2) 3.70 g., b.p. 68–69° (0.8 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4880, $d^{25}{}_{4}$ 1.0892, *MR*D (calcd.) 45.11, *MR*D (found) 44.87; (3) 3.31 g., b.p. 69.0–69.8° (0.8 mm.), $n^{25}{}_{\mathrm{D}}$ 1.4883; and (4) a residue (9.25 g.) composed of 8-nitrohydrindane and higher-boiling products. Fraction 2 (analyzed) exhibited absorption for nitro (6.54 and 7.37 μ) groups (and possibly a *cis* (11.77 and 12.42 μ)[42] ring structure). The product also exhibited minor absorption for nitrite (5.90 μ) and nitrate (6.15 μ) contaminants.[35b] 8-Nitrohydrindane was obtained by nitration of a mixture of *cis*- and *trans*-hydrindanes; b.p. 99.5–101° (4 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4888, $d^{20}{}_{4}$ 1.0857.

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.91; H, 8.88; N, 8.28. Found: C, 64.56; H, 8.91; N, 7.86.

Nitration of *trans*-hydrindane (99.3% *trans*-, 1.0 mole, $n^{25}{}_{\mathrm{D}}$ 1.4616) with refluxing 50% nitric acid (6 moles of HNO_3) resulted in 44% recovery of the initial *trans*-hydrindane[43] ($n^{25}{}_{\mathrm{D}}$ 1.4616;

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(40) The *trans*-9-nitrodecalin exhibited very strong infrared absorption at 10.70, 11.90 and 12.10 μ. This absorption is similar to that observed in *trans*-decalin[38] and may possibly be indicative of the *trans*-decalin ring system.

(41) Since a purpose of these experiments was to convert 9-nitrodecalin to N-9-decalylacetamide in as high a yield as possible in order that a minimal percentage of the major component of each tertiary nitration product could be determined, the 9-decalylamine was not distilled.

(42) *cis*-Hydrindane exhibits infrared absorption at 11.77 and 12.35 μ; *trans*-hydrindane absorbs at 8.50, 11.68 and 11.95 μ. The differences in absorption of the isomeric hydrindanes allow their ready detection and analysis.

(43) Under these conditions *cis*-hydrindane undergoes nitration more rapidly than does *trans*-hydrindane.

the infrared absorptions of the initial and the recovered hydrindanes were identical[43]). 8-Nitrohydrindane[44] was obtained after exhaustive treatment of the nitration product with methanolic sodium methoxide; b.p. 64–65° (0.6 mm.), n^{25}D 1.4875, d^{25}_4 1.089, *MR*D (calcd.) 45.11, *MR*D (found) 44.61; major infrared absorption for $C-NO_2$ (6.54 and 7.37 μ), and possibly *cis* ring[42,43] (11.77 and 12.42 μ) structures, minor absorption for nitrite (5.85 μ) and nitrate (6.10 μ) groups. On the basis of their physical constants and absorption spectra, the 8-nitrohydrindanes obtained from *cis*- and from *trans*-hydrindanes are essentially identical.

Conversion of 8-Nitrohydrindane to 8-Hydrindylamine.—Samples of 8-nitrohydrindane from *cis*- and *trans*-hydrindanes were converted to 8-hydrindylamine by hydrogenation in ethyl ether over Raney nickel. The yields and physical properties of the crude reduction products are listed in Table III. The physical properties and the infrared spectra of the two products were practically the same; there was no absorption for nitro groups in the products.

TABLE III

CONVERSIONS OF 8-NITROHYDRINDANE TO 8-HYDRINDYLAMINE AND TO N-8-HYDRINDYLACETAMIDE

	8-Hydrindylamine[b]		N-8-Hydrindylacetamide	
Parent hydrindane[a]	Yield, %[c]	n^{25}D	Yield, %[d]	M.p., °C.
cis-	98.0	1.4923[e]	83	88
trans-	98.5	1.4925[f,g]	73	88

[a] Hydrocarbon nitrated to give 8-nitrohydrindane. [b] Lit.[f] (from reduction of 8-nitrohydrindane obtained from nitration of a commercial hydrindane) n^{20}D 1.4894. [c] Maximum yield of undistilled 8-hydrindylamine from hydrogenation of 8-nitrohydrindane. [d] Minimum over-all yield of pure N-8-hydrindylacetamide from 8-nitrohydrindane. [e] *MR*D (calcd.) 42.83; *MR*D (found) 42.79. [f] *MR*D (found) 43.00. [g] See S. S. Nametkin, M. R. Rudenko and W. N. Gromova, *Chem. Abstr.*, **37**, 2367 (1943).

Each reduction product was converted to N-8-hydrindylacetamide by reaction with excess acetic anhydride and sodium hydroxide. The crude products as derived from *cis*- and *trans*-hydrindanes were recrystallized from acetone as white crystals in 83 and 73% yields, respectively, of the properties listed in Table III. The N-8-hydrindylacetamides do not depress the melting points of each other. It can be concluded that the tertiary nitration products from *cis*- and *trans*-hydrindanes are essentially similar.

Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.93; H, 10.50; N, 7.73. Found: C, 72.97; H, 10.51; N, 7.64.

The similarity of the samples of crude 8-hydrindylamine was confirmed upon their conversion to N-8-hydrindylbenzamide, m.p. 97.5–98.0°, in excellent yields by reaction with benzoyl chloride and sodium hydroxide; the melting points of the derivatives were not depressed upon admixture.

Anal. Calcd. for $C_{16}H_{21}NO$: C, 79.01; H, 8.64; N, 5.76. Found: C, 79.16; H, 8.83; N, 5.80.

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(44) The mixture of mononitrohydrindanes from nitration of *trans*-hydrindane, 8-nitrohydrindane and secondary nitro-*trans*-hydrindanes, absorbs at 11.77 and 12.42 μ (this absorption is similar to that exhibited by *cis*-hydrindane) and at 8.50 (strong) and 11.95 μ (this absorption is similar to that of *trans*-hydrindane). Upon removing the secondary nitro-*trans*-hydrindanes from the mixture by alkaline extraction, infrared absorption is no longer displayed at 8.50 and 11.95 μ.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, O.]

Assisted Mechanistic Pathways in the Reactions of Organometallic Compounds

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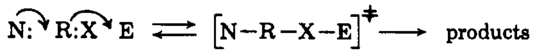
A consideration of the principles underlying the concept of nucleophilic assistance leads to the conclusion that such effects should be most readily observable in the reactions of organometallic compounds in solvents that are poor anion solvators. A model system is proposed, and the concept tested.

Although chemists have, for many years, tended strictly to compartmentalize reaction mechanisms into electrophilic and nucleophilic processes, there has been considerable attention drawn to the fact that some (or all) mechanistic pathways involve both electrophilic and nucleophilic participation.[2]

This is evidenced, for example, in the rates of solvolysis of a number of alkyl and aralkyl halides in a variety of solvents, which are correlated by the Swain equation, $\log k/k_0 = ns_n + es_e$, where n and e are the nucleophilicity and electrophilicity parameters of the solvent, s_n and s_e are sensitivity parameters dependent on the reaction type, and k and k_0 are specific rate constants for the system, and reference system, respectively.[3] The mechanism involved has been represented pictorially by

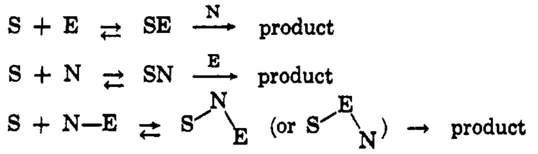


$$\mathrm{N{:}\ R{:}X\ E} \rightleftharpoons [\mathrm{N-R-X-E}]^{\ddagger} \longrightarrow \text{products}$$

(1)

The difficulties associated with the evaluation of the various parameters have been discussed by Gould,[4] but there seems little doubt that both E and N attacks are important in solvolytic reactions.

Bender[5] has pointed out that similar processes are certainly involved in the reaction of carboxylic acid derivatives, and he has described three broad classifications of mechanistic pathways involving these compounds—electrophilic catalysis, nucleophilic catalysis and electrophilic–nucleophilic catalysis.



$$\begin{aligned} &S + E \rightleftarrows SE \xrightarrow{N} \text{product}\\ &S + N \rightleftarrows SN \xrightarrow{E} \text{product}\\ &S + N{-}E \rightleftarrows S\overset{N}{\diagup\diagdown}E \ (\text{or } S\overset{E}{\diagup\diagdown}N) \rightarrow \text{product}\end{aligned}$$

(2)

The word *assistance* might be applied to the actual effect of the so-called catalyst which is involved in the pre-rate-determining equilibrium, since in some cases this substance is not regenerated after the rate-determining process.

It is important to distinguish between complexing, or coördination, and assistance. Complexing, or coordination, focus on the process of replacement of ligand, by ligand. Assistance induces an increased reactivity in an adjacent part of a molecule by a coordination step, and it is this increased reactivity to which attention is drawn in this paper.

Electrophilic assistance has been found in solvolysis reactions of organic halides, Ag^+ and Hg^{2+} serving as the electrophilic assistor, as well as solvent.[6a,b] In protic solvents it is often difficult to observe electrophilic assistance by added solute since few solutes are sufficiently more reactive to make up for differences in concentration between solute and solvent, and the latter serves as an often unseen electrophilic assistor.[6c]

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(1) Alfred P. Sloan Fellow.

(2) For a discussion of the matter see J. Hine "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) C. G. Swain, *et al.*, *J. Am. Chem. Soc.*, **70**, 1119 (1948); **75**, 141 (1953); **77**, 3727, 3731 (1955).

(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt-Dryden, New York, N. Y., 1959.

(5) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

(6) (a) I. Roberts and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 1063 (1937); (b) O. T. Benfey, *ibid.*, **70**, 2165 (1948); (c) C. G. Swain, *et al.*, *ibid.*, **72**, 4578 (1950); **74**, 2534 (1952); **74**, 2538 (1952).