Fractions 1–5 contained material, 0.45 g., the infrared and n.m.r. spectra of which were consistent with bicyclohexenyl. A small amount of this material was reduced and found to have the same infrared spectrum as bicyclohexyl (Eastman Kodak).

Fractions 10–15 contained solid white material, 0.95 g., m.p. 86–90°. The infrared spectrum was consistent with oxetane, with bands in the 930–980-cm.$^{-1}$ region.[11] The n.m.r. spectrum showed strong aromatic (10 protons) and aliphatic (9 protons) bands, as well as bands at δ 4.9 (1 proton) and 3.35 (1 proton). The latter two peaks can be attributed to protons α and β to oxygen in the oxetane ring.[6] The mass spectrum of this material showed a large parent peak at mass 264, which is the calculated molecular weight.

Fractions 21–33 contained material, 1.90 g., whose infrared spectrum was consistent with cyclohexenyldiphenylcarbinol. The n.m.r. spectrum contained bands at δ 7.05 and 7.55 (10 protons), 5.75 (2 protons), 3.4 (1 proton), and 1.3 to 2.1 (7 protons).

The remaining material on the column, 0.65 g., was found to be benzopinacol. The total calculated yields of the reaction were benzopinacol (47%), oxetane (13%), bicyclohexenyl (6% or more), and cyclohexenyldiphenylcarbinol (27%).

Other Photolysis Reactions.—These reactions were carried out as illustrated above for benzophenone and cyclohexene. The total yields of products are given in Table I. Table III gives the physical properties for all new products from these reactions.

Mass Spectrometric Analysis.—The reaction mixtures were reduced by hydrogen over platinum in dioxane. This gave mixtures with the alcohol two mass units higher than the oxetane. The resulting material was introduced into the high-resolution mass spectrometer AEI MS-9 by means of a 210° inlet system. The oxetanes from cyclohexene gave molecular ions at the expected m/e, whose exact mass corresponded to calculated values. (See Table III.) The oxetanes from 1-hexene gave large peaks at the expected mass less 30, corresponding to a loss of formaldehyde.[9] The exact mass of these compounds corresponded to calculated values (Table III). Other hydrocarbon ions were observed which could be due to the dehydration products of the reduced alcohols (Table III).

Acknowledgment.—The author wishes to thank Dr. L. P. Lindeman, who recorded and analyzed the n.m.r. spectra, and Dr. R. H. Teeter for the mass spectrometric analysis.

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(11) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

Correlation of Configuration and Rotatory Direction for Several 4-Substituted Cyclohexenes

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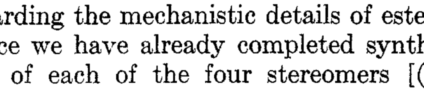
In addition to providing corroboration of the absolute configuration of 4-methylcyclohexene, relative configurations for 4-carboxycyclohexene, 4-hydroxymethylcyclohexene, cyclohexen-4-ylmethyl hydrogen phthalate, and 4-tosyloxymethylcyclohexene were determined and placed on an absolute basis through correlation with 3-methylhexadienoic acid of known absolute configuration.

In order to provide a basis for formulation of a consistent model to account for the details of asymmetric selection during elimination of the original optically active group (AH) from the 4-methylcyclohexyl systems represented by I, reliable information regarding stereochemical arrangements, including absolute correlation between rotational signs[1] and configurations, is required for both the starting systems (Ia–d) and the optically active product, 4-methylcyclohexene (II).



II

Ia, A = –OOCCR′R″R‴
b, A = –NOR′R″
c, A = –SOR′
d, A = –POR′R″

In the carbalkoxy systems, represented by Ia, observation of an asymmetric process (production of optically active II) carries very important implications regarding the mechanistic details of ester pyrolysis.[2] Since we have already completed syntheses and pyrolyses of each of the four stereomers [(+)- and (−)-*cis* and (+)- and (−)-*trans*] of one such system (Ia, A = α-phenylpropionoxy)[3] with definitive assignments of stereochemical details to each, and have observed formation of optically active II during careful pyrolysis of each stereomer,[4] we only required absolute correlation of rotational sign with configuration of the predominant enantiomeric 4-methylcyclohexene obtained in each case.

Despite the fact that it was possible to deduce this information from work already reported,[5] there also appeared to be sufficient justification for additional corroborative experimental work since a question possibly concerning the correctness of the resultant configurational assignment to (+)-4-methylcyclohexene (IIa) was raised recently by Wiberg and Nielsen.[6]

In the course of substantiating the configurational assignments to the enantiomeric 4-methylcyclohexenes during the present work, correlations between rotational signs and configurations were also obtained for several other 4-substituted cyclohexenes.

Partial resolution of 4-carboxycyclohexene (III) was obtained *via* formation and fractional crystallization of the diastereomeric quinine salts, and each enantio-

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(1) All rotatory signs (directions) reported and referred to in this paper are based upon measurements made at the so-called sodium D line (roughly 589 mμ).

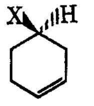
(2) J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. trav. chim.*, **82**, 1123 (1963), and references therein.

(3) For preliminary accounts of this work, see S. I. Goldberg and F-L. Lam, *Tetrahedron Letters*, 1893 (1964); Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 48S.

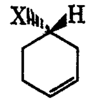
(4) The manuscript containing a full report of these experiments is in preparation.

(5) M. Mousseron, R. Richaud, and R. Granger [*Bull. soc. chim. France*, **13**, 222 (1946)] converted (+)-3-methylcyclohexanone into IIa. The former was subsequently produced from (−)-3-carboxyl-1-cyclohexanol by D. S. Noyce, *et al.* [*J. Am. Chem. Soc.*, **74**, 5912 (1952); **76**, 768, 3630 (1954)], who also, through a series of steps, showed the configurational relationship of (+)-3-methylcyclohexanone and (−)-3-carboxy-1-cyclohexanol to that of (−)-2-methoxyhexane whose relationship to (+)-glyceraldehyde was established earlier by P. A. Levene and co-workers [*J. Biol. Chem.*, **65**, 49 (1925); **67**, 329 (1926); **71**, 465 (1927)]. It should also be noted that Wallach [*Ann.*, **289**, 340 (1896)] obtained (+)-3-methylcyclohexanone from (+)-pulegone, and that the latter was oxidized to (+)-3-methylhexandioic acid by J. v. Braun and F. Jostes [*Chem. Ber.*, **59**, 1091 (1926)]. The relationship of this acid to glyceraldehyde is discussed above.

(6) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).

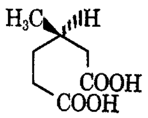


R configuration
a



S configuration
b

II, X = $-CH_3$
III, X = $-COOH$
IV, X = $-CH_2OH$
V, X = $-OOCC_6H_4COOH$
VI, X = $-OTs$



VII

meric acid IIIa and IIIb was directly converted to the corresponding enantiomeric alcohol IVa and IVb, respectively). From the levorotatory alcohol IVb the optically active tosylate VIb was prepared and then converted to *S*-(−)-4-methylcyclohexene (IIb) with a specific rotation (−7.21°), indicating an optical purity of about 7%.[7] This material proved to be unsatisfactory in that it gave rise to a small (20 mg.) amount of 3-methylhexanedioic acid (VII) of such low optical activity that even its rotatory direction could not be reliably determined. The situation was, however, to be expected since it is known that a tenfold decrease in specific rotation occurs in the transformation from II (107°)[8] to VII (9.6°).[9] In order to obtain a suitable sample of optically active II, resolution of *rac*-4-hydroxymethylcyclohexene (IV) was carried out through separation of the diastereomeric strychnine salts formed from the *rac*-hydrogen phthalate half-ester of the carbinol. This provided *R*-(+)-cyclohexen-4-ylmethyl hydrogen phthalate (Va) which, upon reductive cleavage with lithium aluminum hydride, gave IVa with an optical purity about 2.5 times that observed previously in IVb.

Enantiomer IVa was then carried on to *R*-(+)-4-methylcyclohexene (IIa) as before. The dextrorotatory olefin, although still only about 16% optically pure,[7] was nonetheless of much higher optical purity of that observed in IIb (+17.5° *vs.* −7.21°).

Oxidation (ozone and hydrogen peroxide) of IIa to (+)-3-methylhexanedioic acid (VII)[10] then placed the relative configurations established by these transformations on the absolute basis shown in the accompanying structures.

In conclusion, we should like to report the results of one other experiment even though it did not provide any practical contribution.

Following the lead of Brown and his co-workers,[12] we were able to obtained a very partial resolution of *rac*-4-methylcyclohexene (II) by means of incomplete hydroboration with optically active diisopinocampheylborane. Unfortunately, no analysis of this kinetic asymmetric selection process (for the purpose of assignment of absolute configuration)[12] was possible because we were unable to obtain definitive information concerning the orientation of the hydroboration (see Experimental Section).

Experimental Section[13]

***R*-(+)- and *S*-(−)-4-Carboxycyclohexenes (IIIa and IIIb).**—*rac*-4-Carboxycyclohexene[14] (27 g., 0.21 mole) was dissolved in 100 ml. of acetone containing quinine (82 g., 0.25 mole) by gently agitating the warm mixture during 2 hr. After the solution was allowed to cool to room temperature, it was kept in the refrigerator overnight while it slowly deposited the first crop of crystalline salt. Collection and air drying of the salt provided 28 g. of levorotatory material, m.p. 140–142°, $[\alpha]^{26}\mathrm{D}$ −142 ± 0.3° (*c* 3.01, methanol).

This material was dissolved in 150 ml. of fresh acetone and allowed to recrystallize slowly in the refrigerator. This first recrystallization yielded 22 g. of salt, m.p. 142.5–144°, $[\alpha]^{26}\mathrm{D}$ −144 ± 0.4° (*c* 2.57, methanol).

Two more recrystallizations, carried out in the same manner as the first, left 18 g. of levorotatory salt with no significant improvement in either melting point or rotational magnitude, m.p. 142–144°, $[\alpha]^{26}\mathrm{D}$ −146 ± 0.6° (*c* 1.70, methanol).

After treatment of the entire quantity (18 g.) of this salt with 6 *N* hydrochloric acid, the mixture was extracted with four 100-ml. portions of ether, and the combined ethereal extracts yielded, after drying over anhydrous sodium sulfate and evaporation, crude (brown-yellow oil) IIIb (3.8 g., 21% yield), $[\alpha]^{28}\mathrm{D}$ −1.4° (*c* 7.88, methanol), which was directly converted to the corresponding levorotatory carbinol Xb according to the experimental account given below.

The mother liquors obtained from the three recrystallizations of the levorotatory diastereomeric salt described above were combined and evaporated. The residue was taken up in 6 *N* hydrochloric acid, and the resulting mixture was extracted with ether. Examination of the residue (brown-yellow oil), obtained after the dried ethereal solution was filtered and evaporated, indicated crude IIIa, $[\alpha]^{28}\mathrm{D}$ +1.2° (*c* 6.92, methanol), which was reduced to the dextrototatory carbinol Xa without further purification.

***R*-(+)- and *S*-(−)-4-Hydroxymethylcyclohexenes (IVa and IVb). A. From *R*-(+)- and *S*-(−)-4-Carboxycyclohexenes (IIIa and IIIb).**—To 40 ml. of a gently refluxing, ethereal solution of lithium aluminum hydride (2.60 g., 0.068 mole), maintained under a dry nitrogen atmosphere, was added *S*-(−)-4-carboxycyclohexene (IIIb) (3.8 g., 0.030 mole), dissolved in 40 ml. of ether, at such a rate as to maintain the reaction mixture under gentle reflux. The reflux was continued for a 3-hr. period after addition of the ethereal solution was complete. After the reaction mixture was cooled, excess hydride was destroyed by careful addition of water, and the resulting hydrolysate was phase separated. The combined ether extract (four 50-ml. portion) of the aqueous phase was added to the original ethereal phase, and the entire volume was dried over anhydrous sodium sulfate. Evaporation of the ether left an oily residue which, upon fractional distillation, gave IVb (2.5 g., 74% yield): b.p. 62–63°

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[7] Calculation based upon the highest reported specific rotation (+107°)[8] for II.

[8] J. Zelikow, *Chem. Ber.*, **37**, 1374 (1904).

[9] E. J. Eisenbraun and S. M. McElvan, *J. Am. Chem. Soc.*, **77**, 3383 (1955).

[10] 3-Methylhexandioic acid has been configurationally related to glyceraldehyde *via* two pathways. First, as indicated in ref. 5, through pulegone, 3-methylcyclohexanone, etc. This means that the dextrorotatory acid is related to glyceraldehyde and that both are of the *R* configuration. The correctness of this conclusion is evidenced by the second correlation. J. v. Braun and F. Jostes [*Chem. Ber.*, **59**, 1091 (1926)] converted (+)-3-methylhexandioic acid into (+)-1,4-dichloro-2-methylbutane. The levorotatory enantiomer of the latter was subsequently obtained by H. C. Brown, M. S. Kharasch, and T. H. Chao [*J. Am. Chem. Soc.*, **62**, 3435 (1940)] from (−)-2-methyl-1-butanol which has been related to glyceraldehyde by several independent methods.[11]

[11] J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 177 (1954).

[12] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).

[13] Temperature readings are uncorrected. Combustion analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were determined with a Perkin-Elmer, Model 337, grating infrared spectrometer. N.m.r. spectra were recorded on a Varian A-60 spectrometer near room temperature, using chloroform-*d* as solvent with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported under the δ scale in parts per million relative to TMS (0 p.p.m.). Polarimeter measurements were carried out with an O. C. Rudolph and Sons, Inc. (Caldwell, N. J.), instrument, Model 80, using a sodium light source.

[14] Prepared *via* silver oxide oxidation of 4-formylcyclohexene which was purchased from K and K Laboratories, Inc.

(0.6 mm.) (predicted[15] b.p. 220°), lit.[16] b.p. 102° (19 mm.) (predicted[15] b.p. 210°); n^{22}D 1.4822, lit.[16] n^{25}D 1.4828; $[\alpha]^{25}$D 5.80 ± 0.4° (*c* 2.52, methanol).

Similar treatment of the crude *R*-(+)-4-carboxylcyclohexene (IIIa) provided IVb, $[\alpha]^{27}$D +3.08 ± 0.4° (*c* 3.54, methanol).

B. *Via* Formation and Resolution of the Corresponding Hydrogen Phthalate Ester V.—*rac*-4-Hydroxymethylcyclohexene (22.4 g., 0.200 mole), prepared by means of lithium aluminum hydride reduction of *rac*-4-carboxycyclohexene, was heated at 110-115° during 15 hr. in the presence of phthalic anhydride (30.0 g., 0.202 mole) with agitation provided by a magnetically operated stirrer. After the reaction mixture was allowed to cool to room temperature, it was poured into 1000 ml. of a saturated aqueous solution of sodium carbonate and washed with a 50-ml. portion of benzene to remove unreacted neutral starting material. Acidification of the basic aqueous residue with 6 *N* hydrochloric acid produced a mass of crystalline precipitate which was collected in a suction filter and washed with several portions of cold water. The dried, crystalline residue amounted to 36 g. which, after recrystallization from *n*-hexane, produced pure, white, needle-shaped crystals of *rac*-**cyclohexen-4-ylmethyl hydrogen phthalate** (V): 30.6 g. (66.5% yield); m.p. 81.0–82.5°; $\nu_{\max}^{\mathrm{CCl_4}}$ 3400–3200, 3000–2500, 1700 (carboxyl group),[17] 3035, 1605, 1580, 1495, 1450 (*o*-phenylene group),[17] 3020, 1660, 1415, 740–650 (*cis* double bond),[17] 1730, 1290, 1128 cm.$^{-1}$ (aromatic ester)[17]; n.m.r. $\nu^{\mathrm{CDCl_3}}$ δ 12.17 (singlet, $-\mathrm{COO}H$),[18] 7.9–7.4 [complex multiplet, o-$\mathrm{C_6H_4(COO)_2}$],[18] 5.68 (complex multiplet, $-\mathrm{CH_2C}H\!=\!\mathrm{C}H\mathrm{CH_2}-$),[18] 4.24 (doublet, J = 11 c.p.s., $-\mathrm{OC}H_2\mathrm{CH}$),[18] 2.4–1.3 [complex multiplet, $\mathrm{C}H_2\mathrm{C}H\mathrm{(CH_2)C}H_2$-$\mathrm{C}H_2\mathrm{CH\!=\!CH}$].[18]

Anal. Calcd. for $\mathrm{C_{15}H_{16}O_4}$: C, 69.22; H, 6.19. Found: C, 69.15; H, 6.37.

rac-Cyclohexen-4-ylmethyl hydrogen phthalate (V) (30.0 g., 0.114 mole) was added to 150 ml. of a solution of strychnine (38.5 g., 0.115 mole) in 95% aqueous ethanol, and the mixture was warmed during 30 min. to effect complete solution of the components. After the clear solution was allowed to cool to room temperature, it was placed in the refrigerator overnight to allow complete crystallization of the phthalate salts. The diastereomeric salts were separated by means of fractional recrystallization from acetone solution. It was found that from the ninth through twelfth recrystallization no significant improvement in melting point (137–138°) or rotational magnitude, $[\alpha]^{25}$D −6.46 ± 0.2° (*c* 4.15, methanol), had occurred for the levorotatory salt, of which 28 g. was obtained.

***R*-(+)-Cyclohexen-4-ylmethyl hydrogen phthalate** (Va) was obtained from its levorotatory strychnine salt by dissolving the latter (28 g.) in 100 ml. of warm methanol, acidifying the resulting solution by addition of 100 ml. of 20% hydrochloric acid, and extracting the acid mixture with three 100-ml. portions of ether. The ether extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated to a white, crystalline residue. Recrystallization of the residue from 500 ml. of *n*-hexene provided pure, white, needle-shaped crystals (10.8 g., 85.5% yield) of Va, m.p. 82.0-83.5°, $[\alpha]^{25}$D +6.13 ± 0.2 (*c* 3.98, methanol).

To a gently refluxing solution of lithium aluminum hydride (11 g., 0.29 mole) in 150 ml. of anhydrous ether, contained in a dry nitrogen atmosphere, was added an ethereal solution of *R*-(+)-cyclohexen-4-ylmethyl hydrogen phthalate (Va) (10.8 g., 0.041 mole) at a dropwise rate in order to maintain the gentle reflux. The reflux heating was continued during 3 hr. after the addition was complete, and excess hydride was then destroyed by careful addition of cold water to the cooled reaction mixture. The hydrolysate was phase separated, and the mixture of solid and aqueous phases was extracted with two 100-ml. portions of ether. The ether extracts were combined with the original ethereal phase, and the entire volume was dried over anhydrous sodium sulfate. Evaporation of the ether, followed by fractional distillation of the oily residue obtained, provided IVa, 3.65 g. (78.5% yield), b.p. 102–106° (15 mm.), of much higher optical purity, $[\alpha]^{25}$D +13.2 ± 0.3° (*c* 6.48, methanol), than that obtained *via* resolution and reduction of the 4-carboxycyclohexenes (III).

***R*-(+)- and *S*-(−)-4-Tosyloxymethylcyclohexenes (VIa and VIb).**—To a solution of *R*-(+)-4-hydroxymethylcyclohexene (IVa) (3.65 g., 0.0276 mole) in 25 ml. of freshly purified, anhydrous pyridine, maintained near −5° by means of an external ice–salt bath, was added tosyl chloride (*p*-toluenesulfonyl chloride) (5.67 g., 0.0297 mole). The tosyl chloride dissolved after several minutes, and the reaction mixture was then kept in the refrigerator during 24 hr. After the reaction mixture was poured onto 100 ml. of ice and water and the hydrolysate was allowed to warm to room temperature, it was extracted with two 100-ml. portions of ether which were combined and successively washed with cold water, cold dilute hydrochloric acid, and finally cold water again. Evaporation of the dried ethereal solution gave rise to VIa, 6.5 g. (88% yield), as a low-melting solid, m.p. 22–24°, lit.[16] m.p. 23–24°, $[\alpha]^{26}$D +6.73 ± 0.4 (*c* 3.76, methanol).

VIb was prepared in a manner identical with that used for the dextrorotatory material except that the *S*-(−) alcohol, obtained through reduction of the resolved *S*-(−) acid, used was of optical purity much less than that of the *R*-(+) alcohol used above, consequently giving *S*-(−) tosylate VIb of low optical purity, $[\alpha]^{27}$D −2.60 ± 0.4° (*c* 5.46, methanol).

***R*-(+)- and *S*-(−)-4-Methylcyclohexene (IIa and IIb).**—To a stirred solution of lithium aluminum hydride (2.50 g., 0.0658 mole) in 20 ml. of purified diglyme, maintained at 110–115° under a dry nitrogen atmosphere, was added dropwise a solution of *R*-(+)-4-tosyloxymethylcyclohexene (VIa, 6.40 g., 0.0257 mole) in 15 ml. of diglyme. As the reaction progressed, the product was continuously distilled from the reaction mixture and collected in a receiver cooled by a mixture of Dry Ice and acetone. The distillate so obtained was then carefully fractionated, giving IIa: 1.19 g. (51.8% yield); b.p. 102–104°, lit.[5] b.p. 102.5; n^{25}D 1.4410, lit.[6] n^{18}D 1.4449; $[\alpha]^{23}$D +17.5 ± 0.2° (*c* 4.71, methanol), lit.[8] $[\alpha]$D +107.05°. An infrared spectrum (liquid smear) determined from the material was found to be superimposable upon that obtained from authentic *rac*-4-methylcyclohexene.

By means of an identical procedure the *S*-(−)-tosylate VIb of lower optical purity was converted to IIb of correspondingly low optical purity, $[\alpha]^{26}$D −7.21 ± 0.6° (*c* 8.08, methanol).

Partial Resolution of *rac*-4-Methylcyclohexene by Kinetic Asymmetric Selection.—*rac*-4-Methylcyclohexene (57.6 g., 0.700 mole) was added to a stirred diglyme solution of optically active diisopinocampheylborane, prepared[12] by addition of boron trifluoride etherate (0.300 mole, in 75 ml. of diglyme) to a cold (0°) mixture of sodium borohydride (8.55 g., 0.225 mole) and (+)-α-pinene[19] (81.6 g., 0.622 mole) in 150 ml. of diglyme, and the resulting reaction mixture was stirred during 4 hr. at 0°. The reaction mixture was then heated under reduced pressure (25° and 50 mm.), and the distillate so obtained was carefully redistilled, giving the unreacted starting olefin enriched with IIa, 26 g. (90% yield), $[\alpha]^{26}$D +0.70 ± 0.1° (*c* 10.1, methanol).

This sample of dextrorotatory olefin (26 g., 0.27 mole) was similarly treated with another 0.5 equiv. of optically active diisopinocampheylborane, and the unreacted olefin obtained was found to be further enriched with IIa, $[\alpha]^{26}$D +1.11 ± 0.5° (*c* 13.1, methanol). An additional treatment of this material with the optically active hydroboration reagent did not result in an increase in rotational magnitude of the unreacted portion of olefin.

In an attempt to obtain information regarding the orientation of hydroboration in the 4-methylcyclohexene molecule, the hydroborated portion (distillation residue) of the reaction mixture was treated with hydrogen peroxide and aqueous sodium hydroxide to obtain, *via* distillation, followed by gas–liquid partition chromatographic analysis,[20] a mixture of either 3- and 4-

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[15] S. B. Lippincott, *Ind. Eng. Chem.*, **38**, 320 (1945).

[16] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).

[17] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, 1962; L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1958.

[18] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959; G. V. D. Tiers, "Tables of Tau-Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Company, St. Paul, 1958; N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "N.M.R. Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1962; N. S. Bhacca, D. P. Hollis, L. J. Johnson, and E. A. Pier, *ibid.*, Vol. 2, 1963.

[19] The (+)-α-pinene (Glidden Co., Jacksonville, Fla.) used in this experiment was only about 41% optically pure; calculation is based upon comparison of the specific rotation determined from this material, $[\alpha]^{25}$D +19.3 ± 0.1°, and that of the (+)-α-pinene used by Brown, *et al.*,[12] $[\alpha]$D +47.6°.

[20] Carried out with a F and M Scientific Corp. gas chromatograph, Model 500, using a 6 ft. × 0.25 in. column packed with 15% (w./w.) Carbowax 20-M on Diatoport-W at 70° with an inlet He pressure of 52 p.s.i. (flow rate 100 cc./min.).

hydroxy-1-methylcyclohexane and/or the geometric isomers of each. The inability to distinguish among these possibilities rested on the observation that under the best g.l.p.c.[20] conditions used, the retention times determined for the two experimental components (a and b) and those determined for authentic samples of the isomeric alcohols were too close to allow for reliable identification of the position and geometric isomers involved.

Oxidation of *R*-(+)-4-Methylcyclohexene (IIa) to *R*-(+)-3-Methylhexanedioic Acid (VII).—Into a stirred solution IIa (0.680 g., 0.071 mole, $[\alpha]^{23}\text{D}$ +17.5°) in 15 ml. of absolute methanol, maintained near −78° by means of an external Dry Ice–acetone bath, was passed a stream of ozone-enriched oxygen[21] at a rate of nearly 180 cc./min. The ozonation was continued until the color of elemental iodine appeared (*ca.* 2 hr.) in the 300 ml. of 2% aqueous potassium iodide solution through which the stream of gases exciting the reaction mixture was passed. Methanol solvent was then carefully evaporated from the reaction mixture under reduced pressure (1 mm.), leaving a syrupy residue to which 10 ml. of 90% aqueous formic acid and 6 ml. of 30% aqueous hydrogen peroxide were added. The entire mixture was then carefully warmed to about 75° in a water bath, at which time a vigorous effervescence started and continued during about 30 min. The hydrolysate was then concentrated *in vacuo* until formation of a white precipitate was observed. After crystallization was complete, the material was collected on a suction filter, air dried, and recrystallized from benzene, giving VII: 0.31 g. (27% yield); m.p. 87–89°, lit.[9] m.p. 85–89°; $[\alpha]^{26}\text{D}$ +1.3 ± 0.3° (*c* 3.84, chloroform), lit.[9] $[\alpha]^{26}\text{D}$ +9.6° (chloroform).

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[21] Ozone generated with a Welsbach Corp., Philadelphia, Pa., zonator, Style T-23.

Ylide Methylation of Aromatic Nitro Compounds[1]

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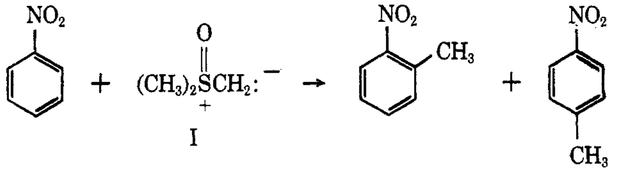
The reaction of dimethyloxosulfonium methylide (I) with nitrobenzene produced *o*- and *p*-nitrotoluenes in about 35% yield with an *ortho/para* ratio of about 10–15. Additional methylation reactions with 1-nitronaphthalene, *o*-, *m*-, and *p*-chloronitrobenzenes, *o*-, *m*-, and *p*-nitrotoluene, and *m*- and *p*-nitroanisoles are described. Some mechanistic possibilities for the origin of the products are considered.

The substitution of an alkyl group for one of the hydrogens in nitrobenzene may be accomplished, *a priori*, by an electrophilic, free-radical, or nucleophilic process, which requires displacement of hydrogen as H+, H·, or H−, respectively. The electrophilic Friedel–Crafts alkylation reaction requires severe experimental conditions or fails with nitrobenzene,[3] while free-radical alkylation[4] of nitro aromatic compounds is accompanied by the formation of by-products including tars. Nucleophilic aromatic alkylation, which requires displacement of hydride ion, is complicated by the fact that carbanions attack the nitro function.[5–8] In addition, carbanion attack on the ring may lead to highly colored substances[9] or condensation products[10] in which the nitro function has been reduced.

In this paper we wish to report the facile methylation of nitrobenzene and substituted nitrobenzenes by a process which appears to occur by aromatic nucleophilic substitution. Metzger, König, and Seelert[11] have published a brief report on the facile methylation of nitrobenzene by the method described in this paper. Their work appeared shortly before completion of this study.

When nitrobenzene and dimethyloxosulfonium methylide (I)[12] were allowed to react at room temperature, a mixture of *o*- and *p*-nitrotoluene (35% yield) was isolated. Identification of the products was accomplished by comparison of retention times in gas–liquid partition chromatography and the infrared spectra with those of authentic samples. The isomer distribution in the product, determined by g.l.p.c., gave an *ortho/para* ratio of about 10–15 and thus revealed a strong tendency for *ortho* isomer formation. After a study of the stability of dimethyloxosulfonium methylide (see Table I), the reaction of nitrobenzene and dimethyloxosulfonium methylide was investigated at various times, temperatures, and concentrations (see Table II).



Since the methylide I possesses carbanionic features and the reaction of carbanions with nitrobenzene can

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[12] This substance was first reported by E. J. Corey and M. Chaykovsky [*J. Am. Chem. Soc.*, **84**, 867 (1962)], who studied the reaction of this reagent with carbonyl compounds. See also subsequent papers.