# Electronic Effects in the Reactions of Olefins with Permanganate Ion and with Osmium Tetroxide

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The oxidation of olefins (alicyclic compounds and stilbenes) by permanganate ion is accelerated by electron-attracting substituents, but these groups retard the reactions of the olefins with osmium tetroxide. For the stilbene oxidations, approximate $\rho$ values obtained were: 0·65 for the permanganate reactions in aqueous dioxan and −0·55 for the osmium tetroxide reactions in dioxan.

THE formation of *cis*-diols, uncontaminated with *trans*-isomers, in the reactions of olefins with permanganate ions or with osmium tetroxide provides good evidence for cyclic intermediates. Using osmium tetroxide, intermediate adducts (I) can often be isolated, especially when tertiary amines are present to act as additional ligands to the metal; hydrolysis normally leads to *cis*-diols in high yield.[1] Intermediates have not been isolated from olefin–permanganate reactions, but the postulated initial species is generally formulated as (II). Yields of diols from permanganate–olefin reactions are generally highest in alkaline solution, *e.g.*, pH above 12.

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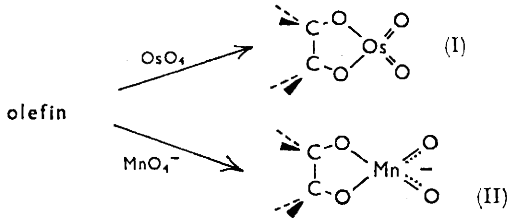
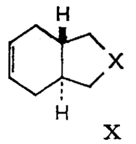
[1] R. Criegee, B. Marchand, and H. Wannowius, *Annalen*, 1942, **550**, 99.

The formation of ketols becomes more pronounced at lower pH's.[2] Study of these reactions can be divided into kinetic and product aspects. In the former, the rate of consumption of olefin provides information concerning the likelihood of the production of the initial cyclic intermediate (I or II). In the latter, the nature of the final organic products can throw light on the stages subsequent to the formation of the cyclic intermediate.



*Rate Studies.*—A competitive method was used. Pairs of related olefins were treated with a deficiency of oxidant, and the mixtures of unchanged starting materials were examined by adsorption or by gas–liquid chromatography. Two general types of compound were studied: substituted stilbenes and substituted alicyclic compounds (III). In order to detect possibly small intramolecular polar effects, it was desirable to use relatively non-polar solvents for the reactions. Cyclopentane could be employed for the reactions of the bicyclic compounds (III) with osmium tetroxide but, for solubility reasons, this was replaced by dioxan for the corresponding oxidations of the substituted stilbenes. As a possible simplification, pyridine was not included in the reaction media (but see final sentence of the Discussion section). For the permanganate oxidations, organic solvents miscible with the aqueous alkaline reagent were required: propan-2-ol and dioxan were used respectively for the alicyclic compounds and for the stilbenes.

*Oxidations of Bicyclic Compounds (III).*—The inductive effect of X [in formula (III)] should be paramount in influencing the reactivity of the olefinic bond, for steric and resonance effects are ruled out by the structural features of this type of molecule.[3]


(III)

| X | Relative rates (±5%)<br>$MnO_4^-$ (in aq. propan-2-ol) | $OsO_4$ (in cyclopentane) |
|---|---|---|
| $CH_2$ | 1 | 1 |
| O | 1·6 | 0·35 |
| $C(OCH_2)_2$ | 1·29 | 0·28 |
| $C(COO^-)_2$ | 0·9 | — |

The results show that permanganate oxidation is accelerated by the electron-attracting ether and acetal groups [$X = O$ and $C(OCH_2)_2$], whereas the converse is true for the osmium tetroxide reactions. The latter result was supported by the relative rates (*ca.* 5 : 1) of the reactions of cholest-5-ene and 3β-chlorocholest-5-ene with osmium tetroxide.

Treatment of the diacid [III; $X = C(CO_2H)_2$] with alkaline permanganate must involve oxidation of the mono- or di-anionic species [III; $X = C(COO^-)(CO_2H)$ or $C(COO^-)_2$], the negative charge of which might be expected to retard the attack of permanganate on the double bond. Such an effect was only just discernible; perhaps much of the negative charge in both reagent and substituent is delocalised by solvation in the aqueous propan-2-ol used.

*Oxidation of Stilbenes.*—

| Substituents | Relative rates (stilbene = 1)<br>$MnO_4^-$ (in aq. dioxan) | $OsO_4$ (in dioxan) |
|---|---|---|
| 4,4′-DiOMe | 1·12, 1·14 | 3·60, 3·76 |
| 4-OMe | 0·89, 0·92 | 1·49, 1·59 |
| Stilbene | 1 | 1 |
| 3,3′-DiOMe | 1·55, 1·63 | 0·80, 0·84 |
| $4-NO_2$ | 7·8 | 0·40, 0·43 |
| $3,3'-DiNO_2$ | 9·5, 10·2 | 0·17 |
| $4,4'-DiNO_2$ | 39 | 0·13 |

These results resemble those from the alicyclic compounds in that permanganate reactions are assisted and osmium tetroxide reactions are inhibited by electron-attracting groups (nitro, *m*-methoxy).

When the permanganate rates ($\log k_s/k$) are plotted against Hammett $\sigma$ values ($2\sigma$ used for disubstituted stilbenes [4]) a picture is obtained in which only the unsubstituted and the *m*-substituted stilbenes fall on a straight line. The results from the 4-nitro- and the 4,4′-dinitro-compounds are closer to the line when $\sigma^-$ instead of $\sigma$ values are used. This requirement, in addition to the positive slope of the graph ($\rho = 0{\cdot}65$), may indicate that the transition state leading to the cyclic type of intermediate (II) has a fractional negative charge on one or both of the benzyl carbons, the charge being delocalised further by a *p*-nitro-group. In this respect the transition state might differ from the initial olefin and from the cyclic intermediate.

Although the 3,3′-dimethoxy-compound appears to be unexceptional in its reactivity, 4,4′-dimethoxystilbene, and, to a lesser extent, 4-methoxystilbene, are more reactive than expected from the $\sigma$-values of these substituents. This behaviour may be the result of a dual mechanism or it may be caused by subtle differences between the substituent effects in this reaction and those involved in the dissociation of benzoic acids. Perhaps the presence of manganese, a transitional element, means that the electronic character of the transition state is particularly flexible. However, deviations from linear free energy relationships have been observed in other reactions of 4-methoxyphenyl compounds.[5]

The reactions between osmium tetroxide and the substituted stilbenes gave a satisfactory Hammett plot with $\rho = -0{\cdot}55$. Again, however, the 4-methoxy- and the

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[2] Cf. K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, 1957, **79**, 2822, where earlier references are given.

[3] Cf. H. B. Henbest, *Proc. Chem. Soc.*, 1963, 159.

[4] Cf. H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 250.

[5] D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 1953, 883; C. G. Overberger and R. W. Cummins, *J. Amer. Chem. Soc.*, 1953, **75**, 4250; C. H. DePuy and D. H. Froemsdorf, *ibid.*, 1957, **79**, 3710; G. Klopman, *Helv. Chim. Acta*, 1961, **44**, 1908; G. Klopman and R. F. Hudson, *ibid.*, p. 1914.

4,4′-dimethoxy-compounds were slightly more reactive than anticipated from the σ-value of this substituent. In the osmium tetroxide–1,2-benzanthracene reaction[6] (performed in chloroform containing 4% pyridine), methoxyl groups had smaller effects on the rate: 9-methoxyl increased it by 15% whereas 9,10-dimethoxyl decreased it by 4%.

*Product studies.* The yields (%) of compounds obtained from the permanganate oxidation of three stilbenes were:

| | Diol | Diketone | Aldehyde | Acid | Total |
|---|---|---|---|---|---|
| 4 4′-Dinitrostilbene ... | 52 | — | 29 | 18 | 99 |
| Stilbene .................. | 14 | 7 | 35 | 25 | 80[a] |
| 4,4′-Dimethoxystilbene | 8 | 33 | 16 | 10 | 67 |

[a] Benzoin (2%) was also obtained. All yields are based on starting materials not recovered.

As racemic hydrobenzoin was recovered (93%) when treated with permanganate under the reaction conditions, the carbonyl compounds (diketone, aldehyde, acid, ketol) must be formed *via* another route or routes from the initial adduct (II).[2] The combined yield of ketone and aldehyde increases at the expense of diol, in the order $p$-NO$_2$, H, $p$-MeO; reactivity increases in the same order in the oxidation of substituted 1-arylethanols by chromic acid.[7]

Yields from the corresponding stilbene–osmium tetroxide reactions were:

| | Diol | Aldehyde | Total |
|---|---|---|---|
| 4,4′-Dinitrostilbene ...... | 32 | 29 | 61 |
| Stilbene ...................... | 48 | 45 | 93[a] |
| 4,4′-Dimethoxystilbene | 37 | 47 | 84 |

[a] Reaction in cyclopentane; the others in dioxan. Yields are based on non-recovered olefins.

The appreciable yields of benzaldehyde obtained under these conditions may be noted. When pyridine was added initially to the stilbene reaction solution, a 90% yield of racemic hydrobenzoin and no benzaldehyde was obtained.

## EXPERIMENTAL

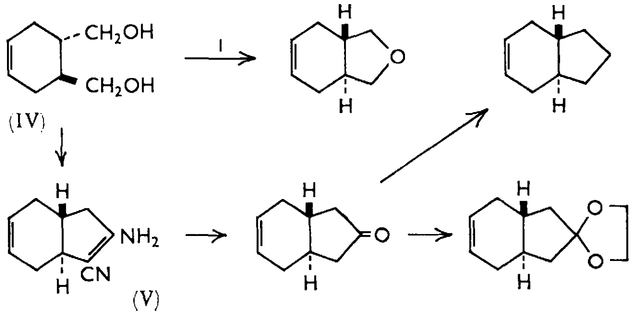
Well purified solvents (cyclopentane, propan-2-ol, and dioxan) were used for the reactions.

*Starting Materials.*—The following stilbenes were made by literature methods:

| Substituents | M. p. | Lit. m. p. | Lit. reference (for method) |
|---|---|---|---|
| 4,4′-Dinitro......... | 300—301° | 280—285° | 8 |
| 3,3′-Dinitro......... | 245—246 | 240—242 | 9 |
| 4-Nitro ........... | 155—156 | 155 | 10 |
| 4,4′-Dimethoxy ... | 211—212·5 | 211 | 11 |
| 3,3′-Dimethoxy ... | 100—101 | 99—100 | 12 |
| 4-Methoxy ......... | 139—140 | 135—135·5 | 13 |

The alicyclic compounds were prepared starting from diol (IV)[14] as outlined on the flow chart. The diacid [III; X = C(CO$_2$H)$_2$] has been reported.[14]

8-*Oxa*-trans-*bicyclo*[4,3,0]*non*-3-*ene*(III; X = O).—Toluene-$p$-sulphonyl chloride (21 g.) was added in portions to a solution of *trans*-4,5-bishydroxymethylcyclohexene (14·2 g.) in boiling pyridine (150 ml.) during 30 min. Heating was continued for 15 min.; the product was then isolated with ether. The crude product in pentane was filtered through alumina (100 g.). Distillation gave the *ether* (7·5 g., 60%), b. p. 59—60°/9 mm., $n_D^{17}$ 1·4854 (Found: C, 77·5; H, 9·6. C$_8$H$_{12}$O requires C, 77·4; H, 9·7%).



Reagent: I, p-Me·C$_6$H$_4$·SO$_2$Cl–pyridine

In a preparative hydroxylation the olefinic ether (1·24 g.) dissolved in propan-2-ol at −9° was treated with sodium permanganate (1·02 g.) dissolved in N-sodium hydroxide (12·8 ml.) during 15 min. Isolation with dichloromethane and crystallisation from ethyl acetate gave material (0·71 g.), m. p. 121—123°. The pure 3β,4β-*dihydroxy*-8-*oxa*-trans*bicyclo*[4,3,0]*nonane* had m. p. 125·5—126·5° (Found: C, 60·7; H, 8·65. C$_8$H$_{14}$O$_3$ requires C, 60·75; H, 8·9%).

trans-*Bicyclo*[4,3,0]*non*-3-*ene*-8-*one* (III; X = CO) *and its Ethylene Ketal*.—*trans*-4,5-Biscyanomethylcyclohexene[14] was isomerised (NaOBu$^t$ in toluene) to give the cyano-enamine (V), m. p. 202—203°, which was hydrolysed by dilute acid to the ketone (III; X = CO), m. p. 63—66°. The moderate yields in each of these stages have been greatly improved recently (Dr. J. Kochling); full details will be submitted for publication soon. A mixture of the ketone (1 g.), toluene-$p$-sulphonic acid (0·3 g.), ethylene glycol (5 ml.), and dry benzene (200 ml.) was distilled slowly. When most of the benzene had distilled, pentane (100 ml.) was added, and the solution was filtered through alumina to give the *ketal* (1·2 g., 90%), m. p. 46—47° (after sublimation) (Found: C, 73·5; H, 9·0. C$_{11}$H$_{16}$O$_2$ requires C, 73·3; H, 8·95%).

trans-*Bicyclo*[4,3,0]*non*-3-*ene* (III; X = CH$_2$).—A solution of the bicyclic ketone (3·3 g.) and 90% hydrazine hydrate (5·5 ml.) in ethylene glycol (40 ml.) was heated under reflux for 1 hr. Water and hydrazine were removed by distillation. Potassium hydroxide (2 g.) was added and the solution heated under reflux for 6 hr. Water (200 ml.) was added to the cold reaction mixture and the solution was extracted with pentane (2 × 200 ml.). Filtration of the pentane extract through alumina (60 g.) and distillation gave the *olefin* (2·2 g., 74%), b. p. 42—44°/11 mm., $n_D^{21}$ 1·4749 (Found: C, 88·2; H, 11·5. C$_9$H$_{14}$ requires C, 88·45; H, 11·55%). Elution of the alumina with ether gave the *azine* of trans-*bicyclo*[4,3,0]*non*-3-*en*-8-*one* (0·15 g., 5%),

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[6] G. M. Badger and K. R. Lynn, *J. Chem. Soc.*, 1950, 1726.

[7] H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.*, 1955, **77**, 4907.

[8] P. Walden and A. Kernbaum, *Ber.*, 1890, **23**, 1959.

[9] P. L'Ecuyer and F. Turcotte, *Canad. J. Res.*, 1947, **25**, 575.

[10] H. Meerwein, E. Buchner, and K. van Emster, *J. prakt. Chem.*, 1939, **152**, 237.

[11] W. Tadros, L. Ekladins, and A. B. Sakla, *J. Chem. Soc.*, 1954, 2351.

[12] K. Kopp, *Annalen*, 1893, **277**, 339.

[13] J. I. G. Cadogan, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 1962, 4164.

[14] D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 1958, 1779.

m. p. 220° (from benzene) (Found: C, 81·0; H, 9·1; N, 10·6. $C_{18}H_{24}N_2$ requires C, 80·55; H, 9·0; N, 10·4%).

*Competitive Permanganate Reactions*.—(i) *Stilbenes*. A solution of sodium permanganate trihydrate (408 mg.) in 0·075N-sodium hydroxide (13 ml.) was added to a solution of stilbene (182 mg.) and 4-nitrostilbene (245 mg.) in dioxan (200 ml.) at 15°. When the purple colour had gone (less than 3 min.) sulphur dioxide was passed in until the solution became clear. Most of the dioxan was removed under reduced pressure. The product were isolated with dichloromethane and the unreacted olefins separated by chromatography on alumina. (Separate experiments showed that stilbenes could be recovered in 96—100% yields from adsorption on alumina.) Representative results using 0·075N-alkali in each experiment:

| Substituents | Starting wts. (mg.) | Recovered wts. (mg.) | $NaMnO_4,3H_2O$ (mg.) | Water (ml.) | Dioxan (ml.) |
|---|---|---|---|---|---|
| H, H ........... | 182 | 157 | 408 | 13 | 200 |
| H, 4-$NO_2$ ...... | 245 | 78 | | | |
| H, H ........... | 362 | 330 | 404 | 13 | 200 |
| 3-$NO_2$, 3′-$NO_2$ | 136 | 56 | | | |
| H, H ........... | 182 | 149 | 260 | 8 | 100 |
| 3-MeO, 3′-MeO | 241 | 175 | | | |
| H, H ........... | 182 | 132 | 262 | 8 | 100 |
| 4MeO, 4′-MeO | 241 | 168 | | | |
| Repeat ......... | 364 | 162 | 1170 | 44 | 300 |
| | 483 | 191 | | | |
| H, H ........... | 366 | 214 | 1013 | 33 | 300 |
| H, 4-MeO ...... | 424 | 259 | | | |
| H, 4-$NO_2$ ...... | 679 | 600 | 409 | 13 | 300 |
| 4-$NO_2$, 4′-$NO_2$ | 138 | 75 | | | |

(ii) *Alicyclic compounds* (III). Anisole, dodecane, and dimethyl adipate are not oxidised by permanganate under the conditions used for the olefin reactions, and they were therefore used as internal standard for g.l.c. analyses. The pair of olefins (1 ml. each) and an internal standard (see below) were dissolved in propan-2-ol at −10° and treated with a deficiency of sodium permanganate in 0·075N-alkali as for the stilbenes.

| Olefins (III) (and internal standard) | Analytical procedure (Pye Argon apparatus: 4 ft. columns containing 100—120 mesh Celite) |
|---|---|
| (*a*) X = $CH_2$ and O (anisole) | 7% Polyphenyl ether at 68° |
| (*b*) X = $CH_2$ and $C(OCH_2)_2$ (dodecane) | 8% Silicone at 75° |
| (*c*) X = O and $C(CO_2H)_2$ (dodecane) (dimethyl adipate) | 8% Silicone at 75° (for ether, X = O)<br>8% Silicone at 90° (for diester *) |

* Unchanged diacid in (*c*) was converted into its dimethyl ester (using diazomethane), and this was estimated against the dimethyl adipate.

*Competitive Osmium Tetroxide Reactions*.—(i) *Stilbenes*. Representative experiment. The tetroxide (403 mg.) in dioxan (10 ml.) was added to a solution of stilbene (360 mg.) and 4-methoxystilbene (212 mg.) in dioxan (40 ml.), and the mixture was stirred at 20° for 4 days. Sodium bisulphite (1·8 g.) in water (30 ml.) and pyridine (35 ml.) was added,[15] and the mixture was stirred for 1 hr. After acidification the products were isolated with dichloromethane and chromatographed on alumina (80 g.) to give stilbene (250 mg.) and 4-methoxystilbene (123 mg.).

(ii) *Alicyclic compounds* (III). The reactions were performed in cyclopentane at 20°. The products were analysed as before by g.l.c.

(iii) *Steroids*. Osmium tetroxide (270 mg.) in cyclopentane (25 ml.) was added to a mixture of cholest-5-ene (401 mg.) and cholesteryl chloride (403 mg.) in cyclopentane (25 ml.) and the mixture stirred for 4 days at 20°. Isolation in ether by the usual procedure, followed by chromatography on alumina (1 kg.) gave cholest-5-ene (214 mg.) m. p. 91—93° and cholesteryl chloride (351 mg.), m. p. 96—98°. Another experiment led to the recovery of cholest-5-ene (208 mg. from 401 mg.) and cholesteryl chloride (351 mg. from 400 mg.).

*Preparative Permanganate Experiments*.—(i) *Stilbene*. The olefin (360 mg.) in dioxan (300 ml.) was treated at 15° with sodium permanganate (605 mg.) in 0·075N-sodium hydroxide (26 ml.). Isolation by standard procedures gave stilbene (202 mg.), rac. hydrobenzoin (26 mg.), m. p. 102—103°, benzil (13 mg.), m. p. 92—94°, benzoin (4 mg.), m. p. 135—137°, and benzoic acid (50 mg.), m. p. 121°. Benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone (172 mg.) from another experiment.

(ii) 4,4-*Dinitrostilbene*. The reaction was performed with the olefin (271 mg.) in dioxan (400 ml.) and sodium permanganate (800 mg.) in 0·075N-sodium hydroxide (32 ml.) to give starting olefin (100 mg.), 4-nitrobenzoic acid (37 mg.), 4-nitrobenzaldehyde (54 mg.), and rac. 4,4′-*dinitrohydrobenzoin* (100 mg.), m. p. 208—209° (Found: C, 55·1; H, 3·95; N, 9·3. $C_{14}H_{12}N_2O_6$ requires: C, 55·3; H, 4·0; N, 9·2%).

Attempted oxidation of rac. 4,4′-dinitrohydrobenzoin (76 mg.) in dioxan (100 ml.) with sodium permanganate (200 mg.) in 0·075N-alkali (11 ml.) gave starting material (69 mg., 91%). Similar experiments with rac. hydrobenzoin and benzoin yielded starting materials (93 and 90% respectively).

(iii) 4,4′-*Dimethoxystilbene*. Oxidation of the olefin (240 mg.) in dioxan (300 ml.) with sodium permanganate (600 mg.) in 0·075N-sodium hydroxide (26 ml.) gave 4-methoxybenzoic acid (30 mg.), m. p. 182—184°, 4,4′-dimethoxybenzil (108 mg.), m. p. 130—131°, 4-methoxybenzaldehyde as its 2,4-dinitrophenylhydrazone (126 mg.), m. p. 247—250°, and rac. 4,4′-dimethoxyhydrobenzoin (27 mg.), m. p. 105—110° (lit.,[16] 113°).

*Preparative Osmium Tetroxide Reactions*.—(i) *Stilbene*. A solution of the tetroxide (244 mg.) and stilbene (180 mg.) in cyclopentane (20 ml.) was kept at 20° for 4 days. Three experiments were worked up in different ways.

(*a*) After treatment with bisulphite in aqueous pyridine [15] benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone (206 mg., 36%).

(*b*) As in (*a*), except that chromatography was used to separate stilbene (36 mg., 20%) and rac. hydrobenzoin (81 mg., 38%) m. p. 102° (impure; see below).

(*c*) Pentane (100 ml.) was added and the mixture was filtered through a pad of dry magnesium sulphate. Benzaldehyde was recovered as its 2,4-dinitrophenylhydrazone (183 mg., 32%) from the filtrate. The yield of derivative was almost unchanged (196 mg., 34%) when the reaction had been initially heated under reflux for 4 days.

(*d*) In a fourth experiment, pyridine (0·5 ml.) was added initially to the reaction mixture. Benzaldehyde was not detected in the filtrate obtained by removal of the solid osmate–pyridine complex. Decomposition of the complex with sodium bisulphite in aqueous pyridine gave, after

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[15] Cf. J. S. Baran, *J. Org. Chem.*, 1960, **25**, 257.

[16] H. D. Law, *J. Chem. Soc.*, 1906, 1512.

chromatography, stilbene (15 mg., 6%) and rac. hydrobenzoin (196 mg., 90%), m. p. 119—120° (lit.,[17] 119—120°).

(ii) 4,4′-*Dinitrostilbene*. A solution of osmium tetroxide (350 mg.) in dioxan (20 ml.) was added to the olefin (136 mg.) in dioxan (230 ml.) and the mixture was stirred for 5 days at 20°. 4-Nitrobenzaldehyde (14 mg. 29%), m. p. 104—105° (from light petroleum) and rac. 4,4′-dinitrohydrobenzoin (49 mg., 32%), m. p. 207—208° (from benzene) were obtained.

(iii) 4,4′-*Dimethoxystilbene*. The olefin (241 mg.) in dioxan (100 ml.), on treatment with osmium tetroxide (400 mg.) in dioxan (20 ml.) for 5 days at 20°, gave 4-methoxybenzaldehyde (297 mg., 47%) and rac. 4-4′-dimethoxyhydrobenzoin (101 mg. 37%), m. p. 110—112°.

*Stability of the Stilbene–Osmium Tetroxide Adduct.*—Solutions of stilbene (360 mg.) in dioxan (30 ml.) and osmium tetroxide (254 mg.) in dioxan (10 ml.) were mixed and kept at 20° for 4 days. 4,4′-Dimethoxystilbene (237 mg.) in dioxan (10 ml.) was then added and the mixture was stirred for 3 days. Isolation as before gave stilbene (180 mg.) and 4,4′-dimethoxystilbene (227 mg.; 96%).

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[17] C. Forst and T. Zincke, *Annalen*, 1876, **182**, 262.