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STUDIES IN CLAISEN REARRANGEMENT—V

ORTHO CLAISEN REARRANGEMENT OF SYMMETRICAL 1,4-DIARYLOXY-TRANS-2-BUTENES

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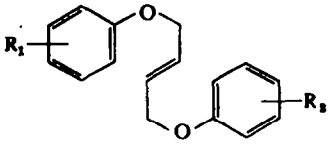
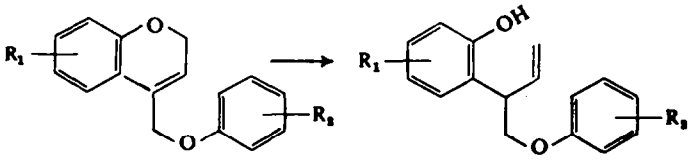
Abstract—The *ortho*-Claisen rearrangement of 1,4-diaryloxy-*trans*-2-butenes has been studied. Synthetic, degradative and spectral evidence is provided for the products of rearrangement. The ability of the butenyl ethers to stop with a single Claisen rearrangement is demonstrated.

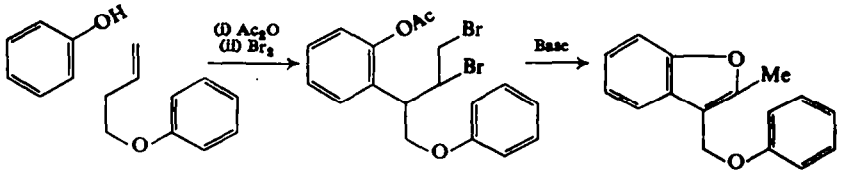
ALTHOUGH the mechanistic features of the *ortho* Claisen rearrangement have been investigated kinetically,[1] the relative roles of the aromatic and the allylic pi systems in the transition state are still not clear. A different approach utilizing product analysis of a molecular system illustrated below has now been investigated.



R_1 and R_2 substituents endow the two aromatic rings with opposing electronic demands producing a system with the following merits: 1. Two aryloxy groups compete for a single allylic system situated symmetrically to both rings. 2. The composition of the products may possibly be decided by a single *ortho* Claisen rearrangement (*vide infra*), as the product is a butenyl ether with respect to the second



aromatic ring, and may resist further Claisen rearrangements, if it does not tautomerize into an allyl ether. 3. The structure of the rearrangement product depicted could be easily verified by conversion into 2-methyl-3-phenoxymethylbenzofuran[2] as follows:



XII XXIX XXX

[1] S. J. RHOADS, *Molecular rearrangements* Chap 11; Interscience, New York (1963).
[2] B. S. Thyagarajan, K. K. Balasubramanian and R. Bhima Rao, *Tetrahedron* **23**, 1893 (1967).

The present study is a preliminary investigation into the behaviour of a number of *symmetrical* 1,4-diaryloxy-*trans*-2-butenes in order to verify the factors described. The synthesis of the symmetrical ethers was achieved through an SN_2 displacement of 1,4-dichloro-*trans*-2-butene with the appropriate phenol. Some of the compounds are reported in the literature while others were prepared for the first time and are listed in Table 1.

TABLE 1. SYMMETRICAL 1,4-DIARYLOXY-*trans*-2-BUTENES

Compound No.	Aryl function	m.p.° or b.p.°/mm	Ref.
I	Phenyl	90	3,4,5
II	O-Chlorophenyl	91	6
III	O-Methoxyphenyl	106	7
IV	O-Methylphenyl	98	3
V	O-Nitrophenyl	150	7
VI	*m*-Methylphenyl	188/5 mm	7
VII	*p*-Chlorophenyl	122	6
VIII	*p*-Methylphenyl	112	5
IX	*p*-Bromophenyl	126	6
X	*p*-Nitrophenyl	154	7
XI	β-naphthyl	154	7

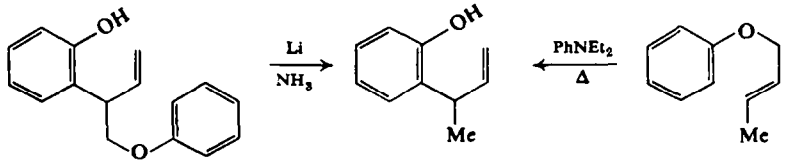
The IR spectra of the 1,4-diaryloxy-*trans*-2-butenes deserve comment. All the ethers show intense absorption in the region of 9 to 11 microns normally attributable to the *trans*-1,2-disubstituted olefins. This could not be put to diagnostic use as the corresponding fully hydrogenated derivatives also show such absorptions. In addition where there were no hydrogens on the olefinic linkage, these absorptions still persisted as in the case of 1,4-di-(*p*-tolyloxy)2,3-dibromo-*trans*-2-butene (XLII).

As most of the butenyl ethers are low melting solids, rearrangement could be studied above the m.p. without solvent but this caused considerable cleavage to the appropriate phenols. Refluxing in a solvent like diethylaniline provided optimal conditions for rearrangement. The yields of products ranged from 50 to 80%. Elemental analyses of the products indicated these were isomeric with the starting ethers. The products, being phenolic in nature, afforded acetyl derivatives but even with a large excess of acetic anhydride, only *mono*acetates were obtained in every case. The acetates showed unsaturation by rapid uptake of bromine in carbon tetrachloride or neutral aqueous permanganate. Ozonolysis of the phenolic products gave formaldehyde—suggesting the presence of a terminal olefine. This unsaturation was not allylic to the second aromatic ring since these compounds resisted further Claisen rearrangements on prolonged heating as proved by the following cleavage experiments.

The rearrangement products on treatment with (a) anhydrous aluminium chloride in refluxing benzene or (b) with methanolic potassium hydroxide or (c) with sodium butoxide in DMSO gave the appropriate phenols from which the starting ethers were derived.

[3] B. S. Thyagarajan, K. K. Balasubramanian and R. Bhima Rao, *Tetrahedron* **23**, 1893 (1967).
[4] B. W. Horrow and H. E. Zaugg, *J. Am. Chem. Soc.* **79**, 1754 (1957).
[5] C. L. Moyle, The Dow Chemical Co., U.S. Patent No. 2,488,499 (1949).
[6] W. Rappe, *Liebigs Ann.* **596**, 5 (1955).
[7] This study.

The structure of the rearrangement product was determined by reduction with lithium in liquid ammonia—the products being identified as phenol and 3-(*o*-hydroxyphenyl)1-butene (XXXII). The latter compound was also obtained by the Claisen rearrangement of phenyl crotyl ether. (XXXI).



XII XXXII XXXI

Additional support for the products of Claisen rearrangement became available from the NMR spectra which showed the following features: (1) A multiplet centred at 4·2 ppm due to the O-methylene and benzylallyl protons. (2) A multiplet centred at 5·2 ppm arising from the terminal methylene and a signal at 6·1 ppm for the vinylic hydrogen. (3) A signal at 9·5 ppm for a phenolic hydrogen. (4) No signals due to aliphatic Me function were present. This observation alone eliminates several alternative structures likely to arise from more than one Claisen rearrangement of the starting butenyl ethers. (5) The NMR Spectrum of the acetate derived from the hydrogenation of the Claisen rearrangement product showed no olefinic protons but only a single Et group, thus confirming the terminal methylene character of the precursor.

In addition to the degradative evidence and spectral data detailed above, synthetic confirmation for the structure was also achieved by three different approaches, Scheme I is illustrated in the accompanying chart.

The phenolic rearrangement product XVIII was converted into its methyl ether (XXVIII) and transformed into the vinyl carbinol (XXXVII) through NBS bromination and hydrolysis. The same carbinol was synthesized from 2-methoxy-5-methylacetophenone (XXXIV) through ω-bromination and stepwise condensation with *p*-cresol and vinyl magnesium bromide. The two carbinols obtained by independent procedures were identical.

Several attempts were made to remove the benzylallyl tertiary OH function so that one could make a direct comparison with the methyl ether XXVIII. Although these attempts were futile, another sequence of reactions was carried out to attain this objective. Colonge *et al.*[8] had earlier described the rearrangement of 1-(*p*-methylphenoxy)4-hydroxy-*cis*-2-butene to give XXXIX. In the present study, the same compound was obtained by rearranging 1-(*p*-methylphenoxy)4-hydroxy-*trans*-2-butene.[9] Methylation of XXXIX, conversion of the primary alcohol into the corresponding bromide followed by treatment with *p*-cresol gave XXVIII which was identical with that obtained by methylation of Claisen rearrangement product XVIII (vide chart II).

The third approach to identify the *ortho* Claisen rearrangement product was its

[8] J. Colonge and G. Des, *Bull. Soc. Chim.* 813 (1959).

[9] We have completed a separate study of the *ortho* as well *para* Claisen rearrangement of 1,4-diaryloxy-*cis*-2-butenes and will report on similar stereoselectivity in product formation in a later communication.

CHART I

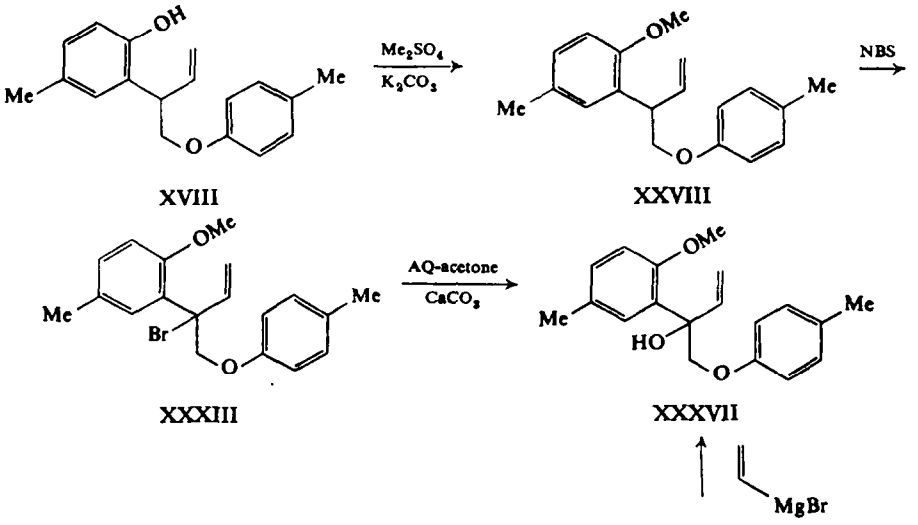
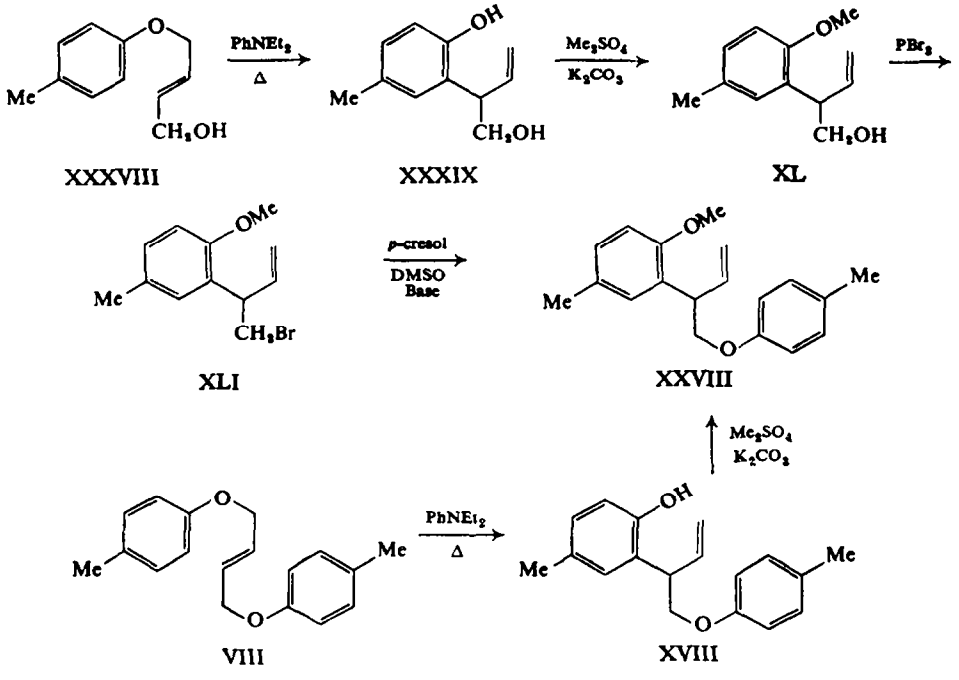


CHART II



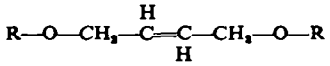
conversion through several steps into the corresponding 2-methyl-3-phenoxymethylbenzofuran as recently described.[2]

The symmetrical 1,4-diaryloxy-*trans*-2-butenes, therefore, undergo normal *ortho* Claisen rearrangement but the rearrangement is not attended by other sequential transformations like ring closures or additional Claisen rearrangements of the second aryl ether moiety. Application of this finding to dissymmetrical ethers in the 1,4-diaryloxy-*trans*-2-butene series, will be presented in a separate publication.

EXPERIMENTAL

Preparation of 1,4-*diaryloxy*-trans-2-*butenes*. In a 3-necked flask fitted with a stirrer and condenser the desired phenol (1·25M) and KOH (1·25M) dissolved in EtOH (100 ml) were refluxed for about 15 min. To this soln, *trans* 1,4-dichloro-2-butene (0·5M) was added slowly, with stirring. After refluxing for about 6 hr it was left overnight. In the case of solid ethers, filtration followed by washing

TABLE 2. SYMMETRICAL 1,4-DIARYLOXY-*trans*-2-BUTENES



No.	R	M.p. or b.p.	Formula	Analysis % Calc C	Calc H	Found C	Found H
I	Phenyl*	88	$C_{16}H_{16}O_2$				
II	O-Chlorophenyl*	91	$C_{16}H_{14}O_2Cl_2$				
III	O-Methoxyphenyl	106	$C_{18}H_{20}O_4$	71·98	6·71	71·38	6·27
IV	O-Methylphenyl*	98	$C_{18}H_{20}O_2$				
V	O-Nitrophenyl	150	$C_{16}H_{14}O_6N_2$	58·18	4·27	58·20	4·27
VI	*m*-Methylphenyl	188/0·55	$C_{18}H_{20}O_2$	80·56	7·51	80·27	7·61
VII	*p*-Chlorophenyl*	122	$C_{16}H_{14}O_2Cl_2$				
VIII	*p*-Methylphenyl*	116	$C_{18}H_{20}O_2$				
IX	*p*-Bromophenyl*	126	$C_{16}H_{14}O_2Br_2$				
X	*p*-Nitrophenyl	154	$C_{16}H_{14}O_6N_2$	58·18	4·27	58·46	4·27
XI	β-naphthyl	154	$C_{24}H_{20}O_2$	84·20	6·30	84·68	5·98

* Reported in lit.

with water and a little alcohol and subsequent crystallization from pet. ether (40–60°) or alcohol gave pure material. Liquid ethers were isolated by removing the alcohol under suction and distilling the residual liquid *in vacuo* (0·5 to 1·0 mm). Table 2 gives a list of the ethers thus prepared including their physical data and analytical values. All the ethers showed the following common features in their NMR spectra: (1) A triplet integrating for 4 protons in the region 4·2 to 4·6 ppm typical of an allylic methylene adjacent to an oxygen. (2) A triplet in the region 6 to 6·2 ppm typical of the vinyl hydrogens.

General procedure for rearrangement. The ether (10 g) was taken in diethylaniline (50 ml) and was refluxed for about 10 hr. The solvent was removed under vacuum (80°/5 mm) and the residue distilled at still lower press (0·5 to 1 mm). Compounds VII and IX were rearranged in ethylene glycol (10 ml for 1 g of ether) and the viscous liquid products were characterized as an acetate deriv. Compound XI on rearrangement in diethylaniline or ethyleneglycol afforded only β-naphthol. The IR spectra of all the rearrangement products showed the presence of a OH function (2·8 μ) and a weak band (6·1 μ) for the newly created unsaturation. Table 3 summarizes data on the rearrangement products. VPC of most of the products showed them to be 90–96% pure.

Attempted pyrolysis of I *and* VII. Compound I (5 g) was heated in Woods-metal bath at 250–270° for 3 hr in CO_2 atm. Fractional distillation of the residue under vacuum gave phenol and another fraction boiling over a wide range. The phenol was identified through its tribromo deriv. Compound VII under similar conditions furnished a little *p*-chlorophenol.

General method for the preparation of acetate derivatives. The phenolic product (5 g) was refluxed in Ac_2O (25 ml) to which pyridine (15 ml) was added, for 6 hr, decomposed with ice pieces, extracted with ether, washed with $NaHCO_3$ aq. and water. The liquid acetates were distilled *in vacuo* while the

solid acetates were crystallized from pet. ether (40–60°) or alcohol. The physical constants and analytical data of the acetates are given in Table 4. IR spectra of all the acetates showed absence of OH peak and the presence of acetyl group (5·72 μ).

Preparation of methyl ethers of XII *and* XVIII. The phenolic product XII or XVIII (0·05M) dissolved in dry acetone (75 ml) to which dry K_2CO_3 (0·05M) was added was refluxed for 15 min.

TABLE 3. REARRANGEMENT PRODUCTS OF SYMMETRICAL DIARYLOXY *trans*-2-BUTENES

Starting compd.	Rearrangement product	yield %	b.p.°/mm	Analysis % Calc C	Calc H	Found C	Found H
I	XII	76	150/0·5	80·00	6·6	79·79	7·14
II	XIII	62	170/0·45	62·15	4·56	62·29	4·51
III	XIV	80	188/0·55	71·98	6·71	72·38	6·95
IV	XV	60	152/0·45	80·56	7·51	80·78	7·75
V	—	—	—	—	—	—	—
VI	XVI	64	174/0·55	80·56	7·51	80·19	7·57
VII	XVII	55	175/0·9*	62·15	4·56	—	—
VIII	XVIII	65	164/0·55	80·56	7·51	80·82	7·62
IX	XIX	50*	—	—	—	—	—
X	—	—	—	—	—	—	—
XI	—	—	—	—	—	—	—

* Characterized as its acetate derivative.

Then Me_2SO_4 (0·075M) was added and refluxing continued for 6 hr. The solvent was removed under sunction, the residue extracted with ether and washed with 10% NaOHaq. Evaporation of the ether furnished a viscous liquid which was distilled *in vacuo*. Table 4 gives the properties of the two methyl ethers and IR spectra of the two compounds showed no OH peak.

Attempted isomerization of XVIII. A mixture of XVIII (17 g) and KOH (70 g) in MeOH (100 ml) was heated in an oil bath at an inside temp of 110–120° for 5 hr. The mixture was cooled, diluted and

TABLE 4. ACETATES OF REARRANGEMENT PRODUCTS

Starting compd.	Acetate	Yield %	b.p. °/mm or m.p.°	Formula (Mono acetate)	Analysis % Calc C	Calc H	Found C	Found H
XII	XX	85	148/0·5	$C_{18}H_{18}O_3$	76·57	6·43	76·33	6·47
XIII	XXI	80	194/0·75	$C_{18}H_{16}O_3Cl_2$	61·53	4·55	61·72	4·42
XIV	XXII	71	210/1·0	$C_{20}H_{22}O_5$	70·17	6·40	70·67	6·59
XV	XXIII	74	182/1·0	$C_{20}H_{22}O_3$	77·39	7·14	77·23	7·28
XVII	XXIV	65	64	$C_{18}H_{16}O_3Cl_2$	61·53	4·55	60·70	4·70
XVIII	XXV	75	75	$C_{20}H_{22}O_3$	77·39	7·14	77·67	6·95
XIX	XXVI	90	70	$C_{18}H_{16}O_3Br_2$	49·09	3·63	48·62	3·82

extracted with ether. The alkaline extract furnished the phenolic product which was distilled, b.p. 96–100°/10 mm, yield 6 g. The IR spectra and VPC of this phenol were identical with that of *p*-cresol. Neutral part could not be characterized.

Base catalysed cleavage of XVIII. To a soln of sodium *t*-butoxide (prepared from Na 2·3 g and *t*-butanol 100 ml) in DmSO (150 ml) XVIII (7·1 g) was added with stirring for 11 hr. The solvent was removed *in vacuo* and the residue decomposed with water, and extracted with ether. The ether extract on washing with 30% NaOHaq yielded a phenolic liquid, b.p. 96–98°/10 mm, yield 2 g. The

IR spectrum and VPC of this phenolic product were identical with those of pure *p*-cresol. The viscous neutral material was not investigated further.

Preparation of phenyl crotyl ether (XXXI). This compound was prepared by the method of Claisen and Tietze.[10]

Preparation of 3-(o-*hydroxyphenyl*)1-*butene* (XXXII). Rearrangement of XXXI according to the procedure of Claisen and Tietze[10] furnished XXXII.

Reductive cleavage of XII *to* XXXII. To liquid ammonia (150 ml) metal (0·45 g) was added with stirring for 15 min. Then a soln of XII (8 g) in ether (25 ml) was added slowly in 15 min. More Li

TABLE 5. METHYL ETHERS OF REARRANGENEMT PRODUCTS

Starting compd.	Methyl ether	Yield %	b.p. °/mm	Formula (Mono ether)	Analysis % Calc C	Calc H	Found C	Found H
XII	XXVII	63	140/0·5	$C_{17}H_{18}O_2$	80·28	7·13	80·24	7·z2
XVIII	XXVIII	58	150/0·4	$C_{18}H_{22}O_2$	80·80	7·80	80·56	7·51

(0·45 g) was added to keep the soln blue in colour and stirring continued for 4 hr. The mixture was decomposed with sat NH_4Claq and extracted with ether. Distillation gave a mobile liquid, b.p. 90–120°/12 mm. The VPC analysis of this liquid product revealed the presence of phenol and XXXII by comparison with authentic specimens.

Allylic bromination of the product XXVIII. A soln of XXVIII (9·4 g) in dry CCl_4 (100 ml) was refluxed gently with N-bromosuccinimide (10·6 g) and a catalytic amount of benzoyl peroxide (0·05 g) for 6 hr and then left overnight. The CCl_4 soln was washed with water and removed under suction leaving pale red viscous liquid (9·6 g) which decomposed on attempted distillation.

Hydrolysis of above bromo compound. A mixture of the above bromo compound (9·6 g) and $CaCO_3$ was suspended in 50% acetone, and refluxed for 12 hr. The reaction mixture was filtered, washed well with ether and the solvents removed. The liquid so obtained was distilled thrice *in vacuo*, b.p. 165–170°/0·5 mm, yield 6 g, 75%. The IR of this liquid was identical with that of vinyl carbinol, obtained by a different route. TLC also showed identical spots.

Synthesis of vinyl carbinol (XXXVII)

(a) *Preparation of* 2-*methoxy-5-methyl-w-bromoacetophenone* (XXXV). This compound was prepared by the method of Pendse and Limaye.[11]

(b) *Preparation of* 2-*methoxy-5-methyl*-w-(p-*methylphenoxy)acetophenone* (XXXVI). A mixture of *p*-cresol (12·09 g), anhyd K_2CO_3 (15·09 g) and the w-bromo compound (16·0 g) were refluxed in EtOH (75 ml) for 5 hr and left overnight. After filtration and washing well with water the product was triturated with alcohol yielding a silky white product which crystallized from alcohol. (15 g, 89%) m.p. 132°. (Found C, 75·51 and H, 6·63. $C_{17}H_{18}O_2$ requires: C, 75·83 and H, 6·71%.) λ_{max}^{KBr} 5·95, 6·23, 6·32, 6·62, 7·33, 7·98, 8·19, 8·66, 9·43, 9·83, 10·02, 10·28, 11·75, 12·21, 12·39, 12·58, 13·53 and 15·53 μ.

(c) *Preparation of vinyl carbinol* (XXXVII). To a soln of vinyl magnesium bromide[12] (20 ml) in dry ether (60 ml) XXXVI (4·3 g) was added and the white suspension was stirred for 6 hr in N_2 atm. Sat. NH_4Claq was added and the mixture extracted with ether. Removal of solvent gave pale yellow viscous liquid, b.p. 168–172°/0·4 mm (3·5 g, 74%). (Found C, 76·41 and H, 7·37%. $C_{19}H_{22}O_2$ requires: C, 76·51 and H, 7·38%.) λ_{max}^{Neat} 2·8, 3·5, 4·1, 6·15, 6·8, 7·0, 7·8, 8·1, 8·7, 9·0, 9·8, 10·1, 10·75, 11·6, 12·4, 13·5 and 14·4 μ.

NMR($CDCl_3$): a doublet at 2·2 ppm (due to 2 ring methyls), a sharp singlet at 3·7 ppm (due to

[10] L. Claisen and Tietze, *Ber. Dtsch. Chem. Ges.* **59**, 2344 (1926).

[11] H. K. Pendse and S. D. Limayu, *Chem. Abstr.* **50**, 11332 (1956).

[12] This soln was prepared according to the procedure of D. Seyforth, *Organic Syntheses* Coll. Vol. IV, page 258. The authors wish to thank Mr. P. S. Venkataramani for providing the soln of known strength.

—OCH_3 protons), a doublet at 4·3 ppm (due to —OCH_3 protons), a triplet centered at 5·3 ppm (due to —CH_2 protons), a triplet centered at 6·35 ppm (due to —CH═ protons) and a multiplet due to aromatic protons.

Synthesis of 3-(2′-*methoxy*-5′-*methylphenyl*)4-(p-*methylphenoxy*)1-*butene* (XXVIII) from XXXIX

(a) *Preparation of* 1-*chloro*-2-*butene*-4-*ol*. This was prepared from 2-butene-1,4-diol.*[8]

(b) *Preparation of* 1-(p-*methylphenoxy*) trans-2-*butene*-4-*ol* (XXXVIII). A soln of *p*-cresol (10·6 g) and KOH (8·4 g) in EtOH (100 ml) was refluxed with the addition of 1-chloro-*trans*-2-butene-4-ol (10·6 g) for 6 hr. It was then extracted with ether, washed well with water and the solvent removed. The yield of desired monocresoxy butene-ol was 5·8 g, 33%, b.p. 156–158°/5 mm.

(c) *Preparation of* 3-(2′-*hydroxy*-5′-*methylphenyl*)1-*butene*-4-*ol* (XXXIX). This was obtained through the Claisen rearrangement of the above 1-(*p*-methylphenoxy) *trans*-2-butene-4-ol.[8]

(d) *Methylation of* XXXIX to XL. Compound XXXIX (20 g) was dissolved in dry acetone (100 ml) to which dry K_2CO_3 (17 g) and Me_2SO_4 (13·5 g) were added and refluxed for 5 hr with stirring and left overnight. It was then filtered, extracted with ether and washed with 10% alkali and water. The residue was distilled *in vacuo*, yield, 12 g, 60%, b.p. 118°/0·6 mm. (Found, C, 75·80 and H, 9·20. $C_{13}H_{16}O_2$ requires: C, 75·40 and H, 9·08%.)

(e) *Preparation of the bromide* XLI. Compound XL (5 g) was mixed with PBr_3 (8·4 g) and left overnight with a guard tube. Next day it was decomposed with ice-water and extracted with ether and washed with water. Removal of solvent *in vacuo* gave XLI (5 g).

(f) *Reaction of the bromide* XLI *with sodium* p-*cresolate to give* XXVIII. *p*-Cresol (5·3 g) was added to a soln of EtONa (prepared from Na 1·1 g and abs EtOH, 25 ml) and the solvent was removed under vacuum. To the dry sodium *p*-cresolate thus obtained, a soln of XLI (5·6 g) in DMSO (20 ml) was added and the mixture was heated on a water bath for 18 hr. It was then extracted with ether, washed with dil. alkali and finally with water. A viscous liquid was obtained from the ether soln and distilled under reduced press, b.p. 170–176°/0·7 mm. The liquid was also chromatographed and eluted with pet. ether (60–80°). The IR and TLC behaviour of this product and XXVIII were identical.

Catalytic hydrogenation on the acetate XX *to the dihydro acetate*

Compound XX (5 g) was dissolved in MeOH (20 ml) and hydrogenated in a Parr hydrogenator at 36 lbs psi with PtO_2 (0·15 g) for 30 min. The catalyst was filtered off, the solvent removed under vacuum and the residue was distilled in *in vacuo*, b.p. 144°/0·2 mm, yield, 4 g. (Found C, 76·05 and H, 6·86. $C_{18}H_{20}O_2$ requires: C, 76·03 and H 7·09%.) NMR ($CDCl_3$): a triplet and a multiplet in the region 0·8 to 1·8 ppm (—CH_2CH_3 protons), a singlet at 2·20 ppm (—$OCOCH_3$ protons), a multiplet at 3·2 ppm (—C*H* Ph protons), a doublet at 4·0 ppm (—OCH_2—CH protons) and a multiplet due to aromatic protons.

Attempted dehydroxylation of the vinyl carbinol XXXVII

(a) The vinyl carbinol XXXVII (3 g) was stirred for 2 hr in liquid NH_3 (100 ml) in the presence of excess of Li (0·028 g) to keep the blue colour throughout the reaction period. It was then decomposed with sat NH_4Claq and extracted with ether. The residue was distilled *in vacuo*, b.p. 94–96/10 mm (fraction I) and b.p. 100–180°/0·8 mm (fraction II). The liquid obtained in fraction I was identified as *p*-cresol by identical IR and VPC spectra with authentic *p*-cresol.

(b) *Zinc dust reduction of* XXXVII. A mixture of XXXVII (1 g) and Zn dust (3 g) was refluxed in EtOH (20 ml of 50%) for 5 hr. The hot soln was filtered, the ppt washed with EtOH and the alcohol removed *in vacuo*. The residue was ether extracted, washed with water and removed. The viscous liquid was distilled under vacuum and the IR spectrum of the product showed a sharp OH peak and was identical with that of the starting material. The starting compound was recovered when the experiment was repeated using Ni–Al alloy instead of Zn dust.

$AlCl_3$ *cleavage of the product* XII. Compound XII (10 g) in dry benzene (100 ml) was refluxed in anhyd $AlCl_3$ (8 g) for 2 hr. The red reaction mixture was decomposed with ice pieces, acidified with HCl and extracted with ether. The ether soln on evaporation gave a red phenolic liquid which distilled at 72–74°/10 mm. It was identified as phenol by VPC and IR spectrum as well as by the tribromo derivative.

* We are thankful to Antara Chemicals, U.S.A., for a generous gift of 2-butene-1,4-diol.

$AlCl_3$ *cleavage of* XVIII. The above experiment was conducted for the compound XVIII. *p*-Cresol (1·5 g) was obtained from XVIII (5·3 g). The VPC and IR spectra were identical with those of authentic *p*-cresol.

Ozonolysis of the product XII. Compound XII (4·8 g) was dissolved in dry $CHCl_3$ (25 ml) and ozone was passed into the soln for 6 hr. The soln was then refluxed with Zn dust (1 g) for 1 hr. The solvent was removed *in vacuo* and the residue steam distilled. The distillate furnished a white deriv with an ethanolic soln of dimedone, m.p. 171°. It did not depress the m.p. of the dimedone derivative of authentic formaldehyde, mixed m.p. 171°. The pot residue after steam distillation was found to be a red viscous liquid which could not be characterized.

Preparation of 1,4-*dichloro*-2,3-*dibromo*-trans-2-*butene*. This was prepared employing 2,3-dibromo-2-butene-1,4-diol,* $SoCl_2$ and pyridine and found to be identical with that reported.[18]

Preparation of 1,4-*di*-(p-*methylphenoxy*)2,3-*dibromo*-trans-2-*butene* XLII. *p*-Cresol (35 g) and KOH (20 g) were dissolved in EtOH (75 ml) and stirred with refluxing with the addition of dichloro-dibromo-butene (24·6 g), for 6 hr. It was filtered and the white needles were washed with water and dried, yield, 14·5 g (50%), m.p. 134–135°. (Found C, 50·68 and H, 4·02. $C_{18}H_{18}O_2Br_2$ requires: C, 50·70 and H 4·23%.) λ_{max}^{KBr} 6·1, 6·25, 6·3, 6·65, 6·92, 7·35, 7·5, 7·6, 7·7, 7·9, 8·25, 8·45, 8·9, 9·0, 9·25, 9·7, 9·9, 10·3, 12·2, 12·7, 14·0, 14·2 and 14·35 μ. NMR ($CDCl_3$): a tall singlet at 2·3 ppm (due to aromatic CH_3 protons), a sharp singlet at 5·0 ppm (due to —OCH_2 protons) and a multiplet centered at 7 ppm due to aromatic protons.

Attempted rearrangement of the ether XLII. The rearrangement of the above ether in diethylaniline afforded no characterizable product.

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[18] A. Valette, *Ann. Chim.* **12**, 644 (1948).