Migration of Double Bonds in End-blocked Linear Olefinic Compounds

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The preparation and the isomerisation of some 1,12-diphenyldodec-6-enes are described. The migration of the double bond in the presence of triethylborane gives an equilibrium between all the positional isomers. The isomer with the double bond conjugated with the aromatic nucleus is preferred but substantial quantities of the other isomers are also present at equilibrium. The concentration of the " conjugated isomer " is very sensitive to steric hindrance but seems to be independent of the inductive effect of substituents on the aromatic rings.

PREVIOUSLY [1] we studied the migration of the double bonds of macrocyclic dienes, in the presence of triethylborane as a catalyst, and the influence of conformational factors on the isomer distribution in equilibrium. Extensive deconjugation of conjugated double bonds in these large rings was observed and interpreted as being due to the particular conformational situation of ring systems.

It was of interest to study double-bond migration in open-chain compounds. We have described the isomerisation of trideca-3,10-diene [1] which was, however, complicated by some exchange between triethylborane and vinylic double bonds formed during the isomerisation. In order to avoid such a complication, straight-chain olefins (VI) were synthesised which carry aromatic end groups (R) so that no vinyl group can be formed during isomerisation. Such olefins were obtained by the following steps: the substituted styrene (I) was prepared by dehydration of the corresponding methanol. The styrene-like molecule was treated with diborane under isomerising conditions.[2] The secondary trialkylborane formed in the first stage of the reaction was thus isomerised to the tri-n-alkylborane (II). Oxidation with hydrogen peroxide [2] gave the 5-phenylpentan-1-ol (III) * which was converted *via* the bromide into 7-phenylhept-1-yne (IV). Reaction of this acetylene with another molecule of the same bromide gave the disubstituted acetylene (V) which was reduced on the Lindlar catalyst to the *cis*-1,12-diphenyldodec-6-ene (VI). The oxidative coupling of 7-phenylhept-1-yne (IV) gave the diyne (VII) which was reduced to the conjugated *cis,cis* diene (VIII) by a method described elsewhere.[4] With substituted aromatic groups possible influence of inductive or steric effects on the equilibrium distribution of isomers could be studied. A series of such substituted diphenyldodecenes with R=C_6H_5–, *p*-Cl·C_6H_4–, *o*-Cl·C_6H_4–, *p*-$CH_3O·C_6H_4$–, *o*-$CH_3O·C_6H_4$–, and 2,4,6-$(MeO)_3C_6H_2$– was isomerised and the results are in Table 1.

para-Substituents with very different inductive effects, such as Cl and OCH_3, give essentially the same equilibrium as the unsubstituted phenyl group, whereas substituents in the *ortho* position have a considerable effect: the concentration of the conjugated isomer (the double bond conjugated with the aromatic nucleus) is then lower than for the *para*-substituted compounds.

The lowest concentration of " conjugated isomer " is obtained from the 2,4,6-trimethylphenyl derivative, where the steric influence of the two *ortho*-methyl groups is most severe (*A*). The decreased stability of the conjugated isomer when the steric requirement of the *ortho* substituent increases is probably due to a torsion of the double bond out of the plane of the benzene ring. The existence of steric hindrance between *o*-methyl

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* This method for the preparation of ω-phenylalkan-1-ols and the corresponding bromide is general and more convenient than the stepwise chain elongation.[3]

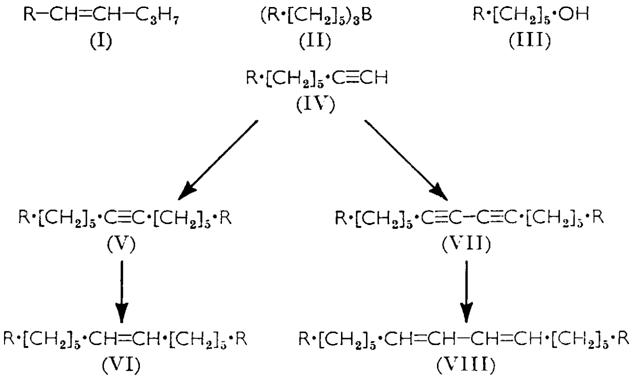
[1] A. J. Hubert and J. Dale, *J. Chem. Soc.*, 1963, 4091.

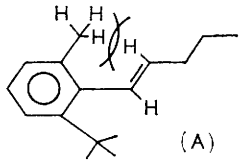
[2] H. C. Brown, " Hydroboration," W. A. Benjamin, Inc., New York, 1962.

[3] J. v. Braun, *Ber.*, 1911, **44**, 2872.

[4] A. J. Hubert, *J. Chem. Soc.*, 1965, 6669.

groups and a side-chain methyl group is well known and, has been demonstrated by the study of the ultraviolet spectra of *o*-methyl- and *o,o*-dimethyl-acetophenone [5] and *ortho*-substituted styrenes.[6] In the case of the 2,4,6-trimethylphenyl derivative this twisting seems to have completely cancelled the conjugation energy, as all isomers are equally important in the equilibrium mixture.





(A)

In the case of a mono-*o*-substituted conjugated isomer, the ***unhindered*** conformer is of a lower energy than any other species including the conjugated *hindered* conformer and similar in energy to the unsubstituted or *para*-substituted conjugated isomer. This unhindered conformer will make the largest contribution to the equilibrium mixture which will be approximately the same as for a system without one large *ortho*-substituent, although not exactly the same as there is now one further form, the hindered conjugated conformer, with an energy approximately the same as for the various unconjugated isomers.

An *ortho*-methoxy-group has less effect in decreasing the concentration of " conjugated isomers " than an *ortho*-chlorine atom: models show that the steric requirement of the former is about the same as of the *ortho*-methyl group, but is much smaller than for the *ortho*-chlorine atom.

The other isomers are present even after long reaction times (Table 1) so that it is safe to assume that a true equilibrium is obtained. Their concentration is about the same (N.B.: the concentration of the symmetrical isomer has a statistical factor of ½); this was to be expected because of the absence of conformational effects from these straight-chain compounds contrary to what happens in the cyclic dienes.[1] Nevertheless, there is a clear tendency for the isomer with one CH_2 group between the double bond and the phenyl group to be somewhat less favoured, except when the conjugated isomer is not favoured (Table 1). No explanation can be offered.

TABLE 1

Isomerisation of $R{\cdot}[CH_2]_5{\cdot}CH{=}CH{\cdot}[CH_2]_5{\cdot}R$ by BEt_3 at 200° to give $R{\cdot}[CH_2]_m{\cdot}CH{=}CH{\cdot}[CH_2]_n{\cdot}R$ ($m + n = 10$)

R	m — n	Distribution of isomers (%) after:					
		2 hr.	4 hr.	8 hr.	16 hr.	24 hr.	32 hr.
$C_6H_5^-$	0—10	3	15	35	43	44	40
	1—9	7	10	10	10	10	11
	2—8	14	16	13	14	14	(17)
	3—7	25	21	13	12	12	12
	4—6	31	23	18	14	13	13
	5—5	20 *	13 *	11 *	7 *	7 *	6 *
2,4,6-$(CH_3)_3C_6H_2^-$	0—10	1	3	5	17	15	19
	1—9	19	21	23	19	20	18
	2—8	20	21	20	17	17	17
	3—7	22	21	20	17	17	18
	4—6	24	22	20	19	20	18
	5—5	14 *	11 *	11 *	10 *	10	10 *
p-$Cl{\cdot}C_6H_4^-$	0—10	9	26	37	42	44	46
	1—9	8	8	9	10	8	8
	2—8	16	15	13	12	12	11
	3—7	25	19	16	14	15	12
	4—6	27	20	17	15	14	16
	5—5	14 *	11 *	7 *	7 *	7 *	8 *
o-$Cl{\cdot}C_6H_4^-$	0—10	3	7	19	26	25	24
	1—9	8	7	10	10	13	12
	2—8	15	15	16	15	15	17
	3—7	24	23	21	18	17	18
	4—6	31	29	22	20	19	19
	5—5	19 *	19 *	12 *	11 *	12 *	10 *
p-$CH_3O{\cdot}C_6H_4^-$ ...	0—10	19	38	46	49	46	50
	1—9	7	8	9	8	9	9
	2—8	15	13	11	11	11	10
	3—7	20	16	13	12	13	12
	4—6	23	17	14	13	13	12
	5—5	12 *	9 *	7 *	7 *	7 *	7 *
o-$CH_3O{\cdot}C_6H_4^-$ ...	0—10	11	30	40	—	—	41
	1—9	13	12	12	—	—	10
	2—8	18	15	13	—	—	13
	3—7	23	17	14	—	—	14
	4—6	24	18	15	—	—	15
	5—5	11 *	8 *	6 *	—	—	6 *

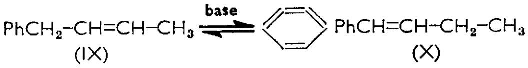
* To be multiplied by a statistical factor of 2.

TABLE 2

Isomerisation of $Ph{\cdot}(CH_2)_m{\cdot}CH{=}CH{-}CH{=}CH{\cdot}(CH_2)_nPh$ ($m + n = 10$) by BEt_3 at 200° for 24 hr.

Starting material	Distribution of isomers (%) after isomerisation					
$m - n$:	0—10	1—9	2—8	3—7	4—6	5—5
$m = 5, n = 5$ ...	22	9	14	19	23	12
$m = 0, n = 10$ ...	30	12	12	14	15	15

The isomerisation of the aromatic olefin (IX) which is similar to the linear mono-olefin (VI; $R = C_6H_5-$) has been studied by Bateman and Cunneen.[7]



There are 80% of the conjugated isomer (X) in the

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[5] E. S. Waight and R. L. Erskine in " Steric Effects in Conjugated Systems," Butterworths Scientific Publications, London, 1958, p. 73.

[6] E. A. Braude, *Experientia*, 1955, **11**, 457.

[7] L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1951, 2283.

mixture at equilibrium. It is very probable that the 20% left are the isomer (IX) because the terminal isomer is thermodynamically very unfavourable.

The ratio of concentrations of (X) : (IX) is about 4 which is the same as the ratio between the conjugated isomer (0—10) and the unconjugated one (1—9) (see Table 1) in the case of the isomerisation of (VIII; R = C_6H_5–). That shows that a true equilibrium is obtained because the catalysts are very different in both cases.

Isomerisation of the diene (VIII; R = C_6H_5) resulted also in a fairly even isomer distribution with the 1,3-diene system essentially intact. That an equilibrium was established was proved by isomerising the " conjugated isomer " Ph–CH=CH–CH=CH·$[CH]_{10}$·Ph. Extensive deconjugation of the 1,3-diene system as such away from the phenyl group took place. Deconjugation of –CH=CH–CH=CH– into –CH=CH·$[CH]_n$·CH=CH– seems to occur only to a small extent. The presence of very small gas-chromatographic peaks owing to the formation of a second homologous series of fragments on ozonolysis [8] indicates such a deconjugation. These results show that conjugation between an aromatic ring and an olefinic system leads to a relatively unimportant stabilisation; between two double bonds much more. On the other hand, that deconjugation of 1,3-dienes in macrocyclic systems does occur to a large extent, proves that particular conformational effects play a much greater role here than in open chains.

TABLE 3

Yields and properties of intermediates and end-products

R	1-Phenylpent-1-ene Yield (%)	1-Phenylpent-1-ene B. p. (°c/mm. Hg)	5-Phenylpentan-1-ol Yield (%)	5-Phenylpentan-1-ol B. p. (°c/mm. Hg)	5-Phenyl-1-bromopentane Yield (%)	5-Phenyl-1-bromopentane B. p. (°c/mm. Hg)
C_6H_5–	80		41	120—130/0·1	50	90—95/0·01
p-Cl·C_6H_4–	74	80—90/0·01	72	131—133/0·1	55	120—125/0·1
o-Cl·C_6H_4–	63	80—90/0·01	66	130—180/0·1	48	120—130/0·1
p-CH_3O·C_6H_4–	48	100/0·1	75	120—133/0·1	40	120—125/0·1
o-CH_3O·C_6H_4	83	74—84/0·01	73	120—157/0·01	44	98—108/0·01
2,4,6-$(Me_3)_3C_6H_2$	80	80—87/0·1	70	120—150/0·01	30	118—122/0·01

R	1-Phenylhept-1-yne Yield (%)	1-Phenylhept-1-yne B. p. (°c/mm. Hg)	1,12-Diphenyldodec-6-yne Yield (%)	1,12-Diphenyldodec-6-yne B. p. (°c/mm. Hg)	1,12-Diphenyldodec-6-ene Yield (%)	1,12-Diphenyldodec-6-ene B. p. (°c/mm. Hg)
C_6H_5–	85	80—85/0·1	44	180—185/0·1	90	180—185/0·1
p-Cl·C_6H_4–	42	100—105/0·01	31	200—220/0·1	90	220—230/0·1
o-Cl·C_6H_4	22	100—105/0·1	23	200—220/0·1	90	210—220/0·1
p-CH_3O·C_6H_4–	57	92—93/0·1	30	200—220/0·1	90	200—220/0·1
o-CH_3O·C_6H_4	53	80—90/0·001	25	170—180/0·01	90	180—184/0·01
2,4,6-$(Me_3)_3C_6H_2$–	45	125—128/0·01	15·5	220—230/0·01	90	200—202/0·01

TABLE 4

Analyses

Compound	Found (%) C	H	O	Cl	Formula	Required (%) C	H	O	Cl
1,12-Diphenyldodec-6-yne	90·9	9·3	—	—	$C_{24}H_{30}$	90·5	9·5	—	—
1,12-Diphenyldodec-6-ene	89·8	9·9	—	—	$C_{24}H_{32}$	89·9	10·1	—	—
1,12-Di-(p-chlorophenyl)dodec-6-yne	73·9	6·9	—	—	$C_{24}H_{32}Cl_2$	74·3	7·25	—	—
1,12-Di-(p-chlorophenyl)dodec-6-ene	74·6	7·6	—	—	$C_{24}H_{32}Cl_2$	74·1	7·7	—	—
1,12-Di-(o-chlorophenyl)dodec-6-yne *	72·7	7·0	—	18·35	$C_{24}H_{28}Cl_2$	74·3	7·25	—	18·45
1,12-Di-(o-chlorophenyl)dodec-6-ene	73·0	7·4	—	18·4	$C_{24}H_{30}Cl_2$	74·4	7·7	—	18·3
1,12-Di-(p-methoxyphenyl)dodec-6-yne	81·3	8·8	9·0	—	$C_{26}H_{34}O_2$	82·5	9·0	8·5	—
1,12-Di-(o-methoxyphenyl)dodec-6-ene	82·4	10·1	—	—	$C_{26}H_{36}O$	82·1	9·5	—	—

* *M*: Found, 375; required, 389.

EXPERIMENTAL

The method of isomerisation and analytical procedure have been described.[1,8]

1,12-*Diphenyldodec*-6-*enes*.—These (except R = 2,4,6-$Me_3C_6H_2$–) were prepared by the following general method: n-Butylmagnesium bromide (1 mole is treated with benzaldehyde (or a substituted benzaldehyde) (1 mole). Dehydration of the crude alcohol at 320—330°/0·1 mm. on a column of alumina gives the corresponding phenylpent-1-enes. The infrared spectrum shows that there is already extensive deconjugation of the double bond away from the aromatic ring: two bands are observed for the *trans* double bond, one at 10·25 μ (conjugated *trans* double bond) and a stronger one at 10·4 μ (isolated *trans* double bond).

This mixture of olefins is dissolved in diglyme (diethylene glycol dimethyl ether) (50 ml.) and diborane [2] is generated by adding $NaBH_4$ (20 g.) in diglyme (125 ml.) to BF_3 ether complex (125 g.) in diglyme (50 ml.). The mixture is then refluxed on an oil-bath at 200° under nitrogen. After 3 hr., the isomerisation is complete [2] and the mixture is dropped slowly into 3N-sodium hydroxide (100 ml.)

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[8] A. J. Hubert, *J. Chem. Soc.*, 1963, 4088.

cooled by ice while 30% hydrogen peroxide (80 ml.) is added slowly.

The infrared spectra of the obtained 5-phenylpentane-1-ols show the presence of OH (bands at 3·0 and 9·6 μ).

Phosphorus tribromide (15 ml.) is slowly dropped into this alcohol and after one night the mixture is poured on crushed ice and extracted with ether. The infrared absorption of OH has disappeared. The obtained 5-bromo-1-phenylpentane is then added to a solution of sodium acetylide in liquid ammonia. After one night dry ammonium chloride is added and ammonia is evaporated. The residue is taken up in ether and water, and worked up to yield the 6-phenylhept-1-yne as a liquid. The infrared spectra show the typical absorption of the monosubstituted acetylenic group at 3·05, 4·7, and 16 μ.

This 7-phenylhept-1-yne is then added to a stoicheiometric amount of sodamide in liquid ammonia, 5-bromo-1-phenylpentane is again added, and after one week the product is worked up to yield the 1,12-diphenyldodec-6-yne. The compound is purified by filtration through a short column of alumina and subsequent distillation. The infrared spectra show no absorption for monosubstituted acetylenes and the disubstituted acetylene absorbs too weakly to be detected.

Reduction on a Lindlar catalyst gives the corresponding 1,12-diphenyldodec-6-ene. The yields, b. p.s, and spectra of these intermediates are in Table 3 and analyses in Table 4. The infrared spectra are similar to the spectra of the acetylenic precursor, except for the absorption of the *cis* double bond at about 14 μ. The purity of these olefins was checked by ozonolysis:[8] one peak corresponding to the expected 6-phenylhexan-1-ol acetate was observed. This method was also used for the identification of the isomers after isomerisation.

In the case of $R = o\text{-}C_6H_4Cl$, the reaction of the bromide with sodium acetylide gave 50% of dehydrobromination besides the expected acetylene (Found: C, 72·9; H, 7·4%. Calc. for $C_{11}H_{13}Cl$; C, 73·0; H, 7·2%). The dehydrobrominated substance boils at 82·83°/0·1 mm. and was identified as a mixture of 5-(*o*-chlorophenyl)pent-1-ene and isomers in which the double bond has migrated into the chain.

Gas chromatography (Megachrom) gave partial separation of two compounds. The first to be eluted is 5-(*o-chlorophenyl*)*pent*-1-*ene* (Found: C, 73·1; H, 7·6%. $C_{11}H_{13}Cl$ requires C, 73·0; H, 7·2%) which gives the typical infrared absorption for a vinyl group at 10·05 and 11·0 μ, while the second fraction absorbs at 10·35 μ, which corresponds to an isolated *trans*-disubstituted double bond.

When $R = p\text{-}CH_3O{\cdot}C_6H_4\text{–}$, a small amount (20%) of $p\text{-}CH_3O{\cdot}C_6H_4{\cdot}[CH]_3{\cdot}CH{=}CH_2$ (plus positional isomers) was isolated as a low-boiling material (b. p. 79—85°/0·1 mm.) during the purification of *p*-methoxyphenylhept-1-yne. This is also formed by dehydrobromination of the bromide during the substitution with sodium acetylide.

1,12-*Bis*-(2,4,6-*trimethylphenyl*)*dodec*-6-*ene*.—Trimesitoyl chloride[9] (0·25 mole) was added to dibutylcadmium[10] (0·15 mole) in benzene to give 2,4,6-trimethylvalerophenone (80%), b. p. 100°/0·1 mm. $\lambda_{max.}$: 5·9 μ (C=O stretching), 6·2 μ (1,3,4,5-tetrasubstituted benzene), 7·25 μ ($-CH_3$), 11·8 μ (CH deformation of a 1,3,4,5-tetrasubstituted benzene). Reduction with $LiAlH_4$ (15 g. = 0·4 mole) in ether (1 l.) gives 1-(2,4,6-trimethylphenyl)pentan-1-ol (90%). The procedure is then the same as the general method.

1,14-*Diphenyltetradeca*-6,8-*diene*.—The preparation has been described.[4]

1,14-*Diphenyltetradeca*-1,3-*diene*.—Benzaldehyde (0·5 mole) was added to n-decylmagnesium bromide (0·55 mole) and a 64% yield of 1-phenylundecan-1-ol was obtained. This alcohol was dehydrated at 350° on alumina *in vacuo* (*ca.* 1 mm.) to give 70% of 1-phenylundec-1-ene.

Treatment with B_2H_6, isomerisation, and oxidation as before gives 11-phenylundecan-1-ol (93%), b. p. 180°/0·1 mm. Treatment of this alcohol (20 g.) with acetic acid saturated with HBr (200 ml.) during one week gives 11-phenyl-1-bromoundecane (12 g. = 52%, b. p. 170—180°/0·01 mm). This compound (12 g. = 0·038 mole) was refluxed with $P(C_6H_5)_3$ (10 g.) in benzene (50 ml.) during one night on an oil-bath. An oil separated after cooling; it was taken up in ether (100 ml.) and treated with butyllithium (26 ml. of a 1·46N solution = 0·038 mole). Cinnamaldehyde (5·1 g. = 0·039 mole) was then added.[11] After one night the solution was hydrolysed and extracted with ether. The solvent was evaporated and the residue purified by chromatography on alumina (*ca.* 300 g.). Fractions of about 20 ml. were collected. Tubes no. 24 and 25 (containing 2·5 and 1·0 g., respectively) contained the diene, which was finally recrystallised, m. p. 45—46·5°, from ethanol (Found: C, 9·02; H, 10·0%. $C_{26}H_{34}$ requires C, 90·1; H, 9·9%). Ozonolysis[8] gave one peak corresponding to $Ph{\cdot}[CH_2]_{11}{\cdot}OAc$. The ultraviolet spectrum showed two strong bands at 212 and 288 mμ (ε 27,400, 34,700).

The raw material after 24 hours' isomerisation gave a complex ultraviolet spectrum with three broad bands at 206, 230—235, and 285 mμ (ε = *ca.* 21,600, *ca.* 9100, *ca.* 6670). These wavelengths agree well with the following chromophores: the phenyl group, an "isolated" conjugated diene $[-CH_2]_m{\cdot}CH{=}CH{-}CH{=}CH{\cdot}[CH_2]_n{-}$ and $Ph{-}CH{=}CH{-}CH{=}CH{-}$.

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[9] Organic Synthesis, 1955, Coll. Vol. III, p. 555.

[10] M. Renson and R. Huls, *Bull. Soc. chim. belges*, 1952, **61**, 599.

[11] U. Schöllkopf, *Angew. Chem.*, 1959, **71**, 260.