# Synthesis and Spectroscopic Properties of 1,4-Diarylbutenynes

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Several new diarylbutenynes have been synthesized and analyses of the n.m.r. and u.v. spectra are described. For planar trans-isomers a conformational preference was found for 1-(α-naphthyl)- but not for 1-(β-naphthyl)-4-aryl-butenynes. This difference is also found between compounds with C-1 attached to the α- or β-position of a larger aryl group.

In a recent paper [1] we reported that irradiation of 1-(α-naphthyl)-4-phenylbut-1-en-3-yne leads to the formation of 1-phenylphenanthrene (Scheme 1). It appeared that some other 1,4-diarylbutenynes, e.g. 1-(3-phenanthryl)-4-phenyl- and 1-(β-naphthyl)-4-(α-naphthyl)-butenyne
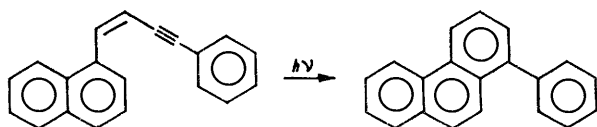
Scheme 1

gave similar photocyclisation products, but that 1,4-diphenylbutenyne did not react on irradiation, and 1-(2-benzo[c]phenanthryl)-4-phenylbutenyne gave only cyclic dimers.

In order to investigate the mechanistic details of the reaction and to establish its scope and limitations a large

spectroscopic properties which give insight into the conformation of this type of compound.

The diarylbutenynes were generally prepared according to the procedure outlined in Scheme 2. An acetal group was substituted in an appropriate arylacetylene (I) and the product (II) was converted into the corresponding arylpropiolaldehyde (III) by acid hydrolysis. The aldehyde was then converted into the desired butenyne (VII) via a Wittig reaction with the triphenylphosphonium salt (VI) of a suitable bromomethyl compound (V), which was itself obtained by side-chain bromination of the corresponding methyl derivative (IV) with N-bromosuccinimide (NBS).

The butenynes formed in this way are cis–trans mixtures (in a ratio from 0.25 to 1.0) from which the trans-isomers and often also the cis-isomers can be obtained in pure form by column chromatography.

Iodine-catalysed isomerisation which is known to
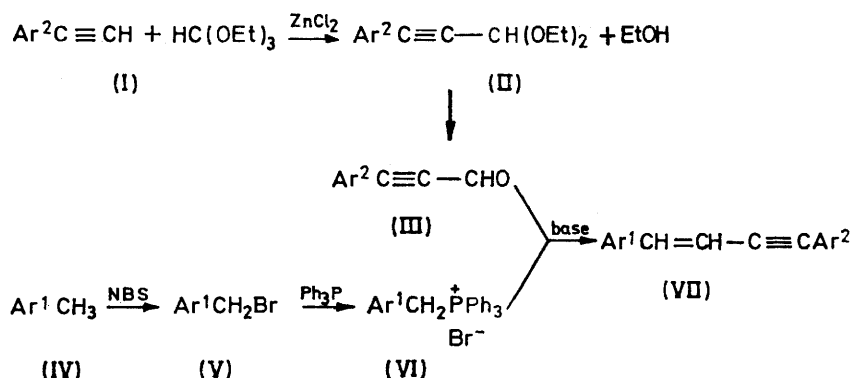
Scheme 2

number of 1,4-diarylbutenynes have been prepared. Their photoreactivity will be discussed in the two following papers.[2] In this paper their synthesis and characterisation is described, together with an analysis of those

convert cis-diaryl-ethylenes [3] and -butadienes [4] into the corresponding trans-isomers is not well suited for the isomerisation of cis-butenynes because of the formation of addition products. These iodobutadienes decompose in

[1] A. H. A. Tinnemans and W. H. Laarhoven, Tetrahedron Letters, 1973, 817.
[2] A. H. A. Tinnemans and W. H. Laarhoven, J.C.S. Perkin II, 1976, 1111, 1115.

[3] W. J. Muizebelt and R. J. F. Nivard, J. Chem. Soc. (B), 1968, 913.
[4] A. J. G. van Rossum, A. H. M. de Bruin, and R. J. F. Nivard, J.C.S. Perkin II, 1975, 1036.

solution and cannot satisfactorily be separated from the butenynes.* Table 1 gives the butenynes synthesized together with their m.p.s and mass spectra. The i.r. spectra of the butenynes in chloroform show besides the characteristic vibrations of the substituents only a weak $v_{C\equiv C}$ absorption at 2 190 cm⁻¹.

N.m.r. Spectra.—The chemical shift of the olefinic protons in diarylbutenyes, δ 5.9—7.8 is always larger

$\Delta\delta$ values for H_a are *ca.* 0.30 p.p.m. because the shielding of H_b in the *trans*-isomers is larger than in the *cis*-isomers whereas this shielding effect for H_a in both isomers is about the same. A smaller difference (*ca.* 0.35 p.p.m.) is found for 1-naphthylbutenynes (7), (8), and (10), which may have a slightly distorted planar conformation in the *trans*-configuration.

The spin–spin coupling constants of the olefinic protons

TABLE 1

M.p.s and mass spectra of 1,4-diarylbutenynes Ar¹CH=CH–C≡CAr [2]

Compound		Ar¹	Ar²	M.p. (°C)	m/e (%) [a]
(1a)	cis	2-Naphthyl	H	108—110	
(1b)	trans	2-Naphthyl	H	80.5—82	178 (100)
(2a)	cis	2-Naphthyl	Me	69—73	
(2b)	trans	2-Naphthyl	Me	96—98.5	192 (100)
(3a)	cis	2-Naphthyl	Phenyl	96—97	
(3b)	trans	2-Naphthyl	Phenyl	131—132	254 (100)
(4)	trans	2-Naphthyl	1-Naphthyl	115—116	304 (100)
(5a)	cis	2-Naphthyl	3,5-Dimethylphenyl	90—91	
(5b)	trans	2-Naphthyl	3,5-Dimethylphenyl	85—87	282 (100)
(6)	trans	8-Phenyl-2-naphthyl	Phenyl	133.5—135	330 (100)
(7a)	cis	1-Bromo-2-naphthyl	Phenyl	59—61	
(7b)	trans	2-(1-Bromonaphthyl)	Phenyl	107—109	332/334 (21), 253 (100)
(8a)	cis	1-Naphthyl	Phenyl	85—86	
(8b)	trans	1-Naphthyl	Phenyl	112—113	254 (72), 253 (100)
(9)	trans	1-Naphthyl	1-Naphthyl	143—146	304 (100)
(10a)	cis	4-Methyl-1-naphthyl	Phenyl	104.5—106	
(10b)	trans	4-Methyl-1-naphthyl	Phenyl	115—116	268 (77), 252 (100)
(11)	trans	4-Hydroxymethyl-1-naphthyl	3,5-Dimethylphenyl	133—134.5	312 (100)
(12)	trans	4-Methoxycarbonyl-1-naphthyl	3,5-Dimethylphenyl	90—92	340 (100)
(13a)	cis	2-Methyl-1-naphthyl	Phenyl	107—108	
(13b)	trans	2-Methyl-1-naphthyl	Phenyl	47—49	268 (51), 252 (100)
(14)	trans	Phenyl	Phenyl	99—101	204 (100)
(15)	trans	Phenyl	1-Naphthyl	96—98	254 (100)
(16)	trans	*p*-Methoxyphenyl	Phenyl	98—99	234 (100)
(17)	cis	3,5-Dimethylphenyl	Phenyl	75—76	232 (100)
(18a)	cis	3-Phenanthryl	Phenyl	111—113	
(18b)	trans	3-Phenanthryl	Phenyl	143—146	304 (100)
(19a)	cis	3-Phenanthryl	3,5-Dimethylphenyl	76—78	
(19b)	trans	3-Phenanthryl	3,5-Dimethylphenyl	159.5—161	332 (100)
(20)	trans	1-Phenyl-9-phenanthryl	Phenyl	120—124	380 (100)
(21)	trans	1-(3,5-Dimethylphenyl)-9-phenanthryl	3,5-Dimethylphenyl	166—168	436 (100)
(22a)	cis	5,7-Dimethyl-3-phenanthryl	3,5-Dimethylphenyl	96—98	
(22b)	trans	5,7-Dimethyl-3-phenanthryl	3,5-Dimethylphenyl	140—142	360 (51), 345 (100)
(23a)	cis	2-Benzo[c]phenanthryl	Phenyl	Oil	
(23b)	trans	2-Benzo[c]phenanthryl	Phenyl	94—97	354 (89), 278 (100)
(24)		1-(1-Naphthyl)-2-phenylethynylcyclohexene		75—77	308 (100)

[a] Molecular ions and base peak of *trans*-compounds.

than that generally found for olefinic protons, δ 4.5—6.0. The additional downfield shift is due to interactions of the olefinic bond with the aryl groups. For H_b this effect is reduced by the shielding influence of the nearby acetylene bond, so that the signal from this proton always has the lower δ value. As a consequence of less deshielding on the non-planar *cis*-compounds the peaks of the olefinic protons of *cis*-isomers are always at higher field than those of *trans*-isomers; an exception is (13) where a planar conformation is also prevented in the *trans*-isomer. The difference between the δ values for H_b in *cis*- and *trans*-isomers ($\Delta\delta$) is *ca.* 0.5 p.p.m. for most of the isomer pairs. The same difference is found for the olefinic protons in *cis*- and *trans*-stilbenes.[6,7] The

(J_{cis} 12.0 $\pm$ 0.5, J_{trans} 16.0 $\pm$ 0.5 Hz) show the same ratio (0.75) as found for stilbenes.[6,7]

The olefinic proton signals of most of the *trans*-4-aryl-1-(2-naphthyl)butenynes (3)—(6) do not vary much (H_a: δ *ca.* 7.05; H_b: δ *ca.* 6.35). The introduction of a large substituent at C-1, as in (7) causes, however, a large downfield shift for H_a (δ 7.61), whereas H_b remains unchanged (δ 6.34). The reason is that in the unsubstituted 1-(2-naphthyl)butenynes the planar conformations (A and B) are fairly equivalent whereas in the 2-(1-bromonaphthyl) derivative the less hindered conformation A, having H_a in the neighbourhood of the bromine atom, predominates.

* After treatment of a mixture of *cis*- and *trans*-(4) with iodine, besides (3b), *cis,trans*-1,2-di-iodo-1-α-naphthyl-4-β-naphthyl-butadiene was isolated, m.p. 157—159 °C, m/e 510, δ 7.05 and 7.20 (part AB, J_{AB} 15 Hz), 7.21—7.57 (7 H, m), and 7.62—7.90 (8 H, m) (see ref. 5).

[5] A. A. Petrov, I. I. Porfir'era, I. I. Iakovleva, and K. S. Mingleva, *J. Gen. Chem. (U.S.S.R.)*, 1958, **28**, 2357.

[6] M. H. de Jong and W. H. Laarhoven, *Rec. Trav. chim.*, 1973, **92**, 673.

[7] H. Güsten and M. Salzwedel, *Tetrahedron*, 1967, **23**, 173, 187.

TABLE 2

N.m.r. spectra (δ) of 1,4-diarylbutenynes, $Ar^1CH_a=CH_b-C\equiv C-Ar^2$ taken in CS_2

Compound	H_a	H_b	Ar^1 H	Unresolved aromatic protons	Ar^2 H	Substituent protons
(1a)	6.71	5.65	8.05 (s, H-1), 7.97 and 7.66 (AB, H-3, -4, J_{AB} 8.3 Hz), 7.58—7.74 (m, H-5, -8), 7.24—7.43 (m, H-6, -7)			
(1b)	7.06	6.13		7.30—7.82 (7 H, m)		3.25 (s, methine) 2.92 (s, methine)
(2a)	6.56	5.61	8.04 (s, H-1), 7.99—7.67 (AB, H-3, -4, J_{AB} 8.4 Hz), 7.58—7.76 (m, H-5, -8), 7.18—7.42 (m, H-6, -7)			2.02 (s, CH_3)
(2b)	6.87	6.13	7.54—7.82 (m, H-1, -4, -5, -8), 7.28—7.54 (m, H-3, -6, -7)			1.96 (s, CH_3)
(3a)	6.72	5.88	7.99 and 7.68 (AB, H-3, -4, J_{AB} 8.4 Hz), 7.58—7.79 (m, H-5, -8)	7.16—7.48 (7 H, m)		
(3b)	7.03	6.35	7.56—7.79 (m, H-1, -5, -8), 7.46 and 7.62 (AB, H-3, -4, J_{AB} 8.5 Hz)	7.16—7.53 (7 H, m)		
(4)	7.19	6.54		7.30—7.83 (13 H, m)	8.31 (m, (H-8)	
(5a)	6.71	5.87	8.19 (s, H-1), 8.02 and 7.64 (AB, H-3, -4, J_{AB} 8.5 Hz), 7.57—7.78 (m, H-5, -8), 7.23—7.44 (m, H-6, -7)		7.03 (s, H-2, -6), 6.86 (s, H-4)	2.26 (s, $2CH_3$)
(5b)	7.03	6.37	7.64 (s, H-1), 7.21—7.46 (m, H-3, -6, -7), 7.46—7.78 (m, H-4, -5, -8)		6.99 (s, H-2, -6), 6.84 (s, H-4)	2.25 (s, $2CH_3$)
(6)	6.92	6.25	7.60—7.68 (m, H-4, -5, -1), 7.47 (d, H-3)	7.12—7.34 (7 H, m)		7.35 (s, C_6H_5)
(7a)	7.16	5.99	8.37 and 7.58 (AB, H-3, -4, J_{AB} 8.5 Hz), 7.53 (m, H-5), 8.20 (m, H-8)	7.05—7.45 (7 H, m)		
(7b)	7.61	6.34	8.26 (m, H-8)	7.19—7.73 (10 H, m)		
(8a)	7.31	6.04	8.19 (d, H-2), 7.62—7.82 (m, H-4, -5), 7.93 (m, H-8)	7.10—7.50 (8 H, m)		
(8b)	7.68	6.34	7.57—7.82 (m, H-4, -5), 8.03 (m, H-8)	7.18—7.57 (9 H, m)		
(10a)	7.28	5.99	8.11 (d, H-2), 7.89 (m, H-5), 7.95 (m, H-8)	7.07—7.49 (8 H, m)		2.64 (s, CH_3)
(10b)	7.66	6.28	7.87 (m, H-5), 8.02 (m, H-8)	7.11—7.53 (9 H, m)		2.65 (s, CH_3)
(11)	7.80 [a]	6.43	7.40—7.69 (m, H-2, -3, -6, -7), 8.21 (m, H-5), 8.12 (m, H-8)		7.18 (s, H-2, -6), 6.99 (s, H-4)	5.12 (s, CH_2), 2.33 (s, $2CH_3$), 1.90 (s, OH)
(12)	7.63	6.36	7.47 and 8.00 (AB, H-2, -3, J_{AB} 7.9 Hz), 8.98 (m, H-5), 7.38—7.54 (m, H-6, -7), 8.01 (m, H-8)		7.01 (s, H-2, -6), 6.83 (s, H-4)	3.83 (s, OCH_3), 2.21 (s, $2CH_3$)
(13a)		6.19	7.61 (d, H-4), 7.70 (m, H-5), 7.88 (m, H-8)	6.71—7.42 (9 H, m)		2.46 (s, CH_3)
(13b)	7.24	6.00	7.66 (m, H-5), 8.00 (m, H-8)	7.11—7.47 (9 H, m)		2.45 (s, CH_3)
(9)	7.81	6.48	8.06 (m, H-8)	7.20—7.80 (12 H, m)	8.35 (m, H-8)	
(14)	6.87	6.24		7.07—7.42 (10 H, m)		
(15)	7.01	6.39		7.10—7.78 (11 H, m)	8.29 (m, H-8)	
(16)	6.81	6.08	6.68 and 6.74 (part AB, H-2, -6, J_{AB} 6.5 Hz)	7.12—7.38 (7 H, m)		3.70 (s, OCH_3)
(17)	6.50	5.74	7.42 (s, H-2, -6), 6.82 (s, H-4)		7.15—7.39 (5 H, m)	2.27 (s, $2CH_3$)
(18a)	6.82	5.95	7.71—7.90 (AB, H-1, -2, J_{AB} 8.3 Hz), 9.27 (s, H-4), 8.48 (m, H-5), 7.72 (m, H-8), 7.58 (s, H-9, -10)	7.21—7.56 (7 H, m)		
(18b)	7.16	6.46	8.47 (s, H-4), 8.55 (s, H-5)	7.18—7.83 (12 H, m)		
(19a)	6.76	5.93	9.33 (s, H-4), 8.50 (m, H-5), 7.56 (s, H-9, -10)	7.26—7.88 (5 H, m)	7.06 (s, H-2, -6), 6.85 (s, H-4)	2.21 (s, $2CH_3$)
(19b)	7.12	6.43	8.42 (s, H-4), 8.50 (m, H-5), 7.55 (s, H-9, -10)	7.33—7.79 (5 H, m)	7.02 (s, H-2, -6), 6.83 (s, H-4)	2.24 (s, $2CH_3$)
(20)		6.16	8.56 (m, H-4), 8.64 (m, H-5), 8.08 (m, H-8), 7.88 (s, H-10)	7.14—7.72 (10 H, m)		7.43 (s, C_6H_5)
(21)	7.59	6.15	7.31 (d, H-2), 7.52 (t, H-3), 8.49 (d, H-4), 8.58 (m, H-5), 7.43—7.64 (m, H-6, -7), 8.05 (m, H-8), 7.90 (s, H-10)	6.98 (5 H, s), 6.80 (1 H, s)		2.33 (s, $2CH_3$), 2.21 (s, $2CH_3$)
(22a)	6.80	5.89	9.11 (s, H-4), 7.72 and 8.00 (AB, H-1, -2, J_{AB} 8.3 Hz), 7.00 (s, H-9, -10), 7.38 (s, H-8), 7.12 (s, H-6)		6.91 (s, H-2, -6), 6.82 (s, H-4)	2.97 (s, CH_3), 2.46 (s, CH_3), 2.22 (s, $2CH_3$)
(22b)	7.09	6.35	7.39 (s, H-8), 7.19 (s, H-6), 8.64 (s, H-4), 7.57 and 7.67 (AB, H-1, -2, J_{AB} 8.5 Hz), 7.48 (s, H-9, -10)		6.97 (s, H-2, -6), 6.82 (s, H-4)	3.03 (s, CH_3), 2.44 (s, CH_3), 2.24 (s, $2CH_3$)
(23a)	6.77	5.90	9.50 (s, H-1), 8.02 and 7.77 (AB, H-3, -4, J_{AB} 8.1 Hz), 9.00 (m, H-12)	7.04—7.36 (8 H, m) 7.50—7.86 (4 H, m)		
(23b)	7.15	6.41	8.87 (s, H-1), 8.91 (m, H-12)	7.16—7.92 (14 H, m)		
(24)			7.57—7.86 (m, H-4, -5, -8)	7.14—7.44 (4 H, m), 6.83—7.02 (3 H, m), 6.52—6.70 (2 H, m)		2.36—2.64 (4 H, m), 1.78—2.06 (4 H, m)

[a] Measured in $CDCl_3$.

The same is true for the corresponding *cis*-isomers. In (7a) H_a is shifted much further downfield than H_b in comparison with (3a), and naphthyl H-3 shows a strong downfield shift due to the nearby acetylene group whereas H-8 has about the same δ values as in (7b).

A comparison of the δ-values of the olefinic protons in *trans*-4-aryl-1-(1-naphthyl)butenynes (8)—(12) with those of the 1-(2-naphthyl) derivatives reveals that again the H_b signal is at *ca.* 6.35 but that H_a is at δ *ca.* 7.7 instead of 7.05. Apparently for the 1-(1-naphthyl) derivatives there is always a preference for the conformation C which shows less steric hindrance than D.

The introduction of a substituent (CH_3) at C-2 as in (13b) now causes an upfield shift for both olefinic protons due to a shielding effect of the naphthyl residue as a

(3b) X = H
(7b) X = Br

(8b) X = H
(13b) X = CH₃
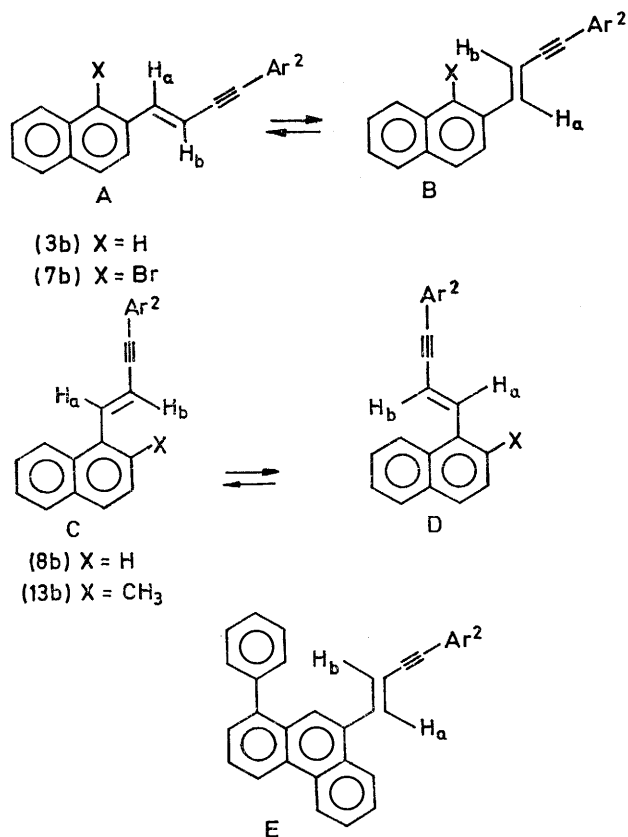
consequence of rotation around C-1-C_α which relieves steric interaction. In accordance with this explanation the shift is larger for the H_a signal than for that of H_b. A similar result as found for the 1-(1-naphthyl)butenynes is obtained with (20) and (21). Both these show an upfield shift for the H_b signal but not for that of H_a by comparison with those for (5b), (18b), and (19b), indicating that only H_b is shielded by the phenyl substituent as in conformation E.

Examination of the n.m.r. spectrum of (23a) proved interesting in view of the preference for the pre-helicene *cis-syn*- over the *cis-anti*-conformation which was previ-

[8] R. H. Martin, N. Defay, H. P. Figeys, K. Lé Van, J. J. Ruelle, and J. J. Schurter, *Helv. Chim. Acta*, 1972, **55**, 2241.

ously found for *cis*-1-aryl-2-(benzo[*c*]phenanthryl)ethylenes [6,8] and other complex, phenyl substituted diarylolefins.[9] Apparently such a conformational preference does

(23a)(*cis - syn*)   (*cis - anti*)
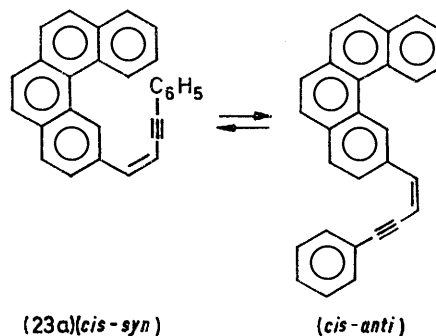
not occur in (23a) since the H-1 and -3 signals are shifted to a similar extent by the acetylene bond to lower field values (0.50—0.90 p.p.m.) by comparison with (23b) and since H-3, a β-proton in the *trans*-isomer, is certainly to the upfield side of the complex unresolved pattern for this compound. All other aromatic protons have nearly the same δ values for both isomers. Moreover the n.m.r.
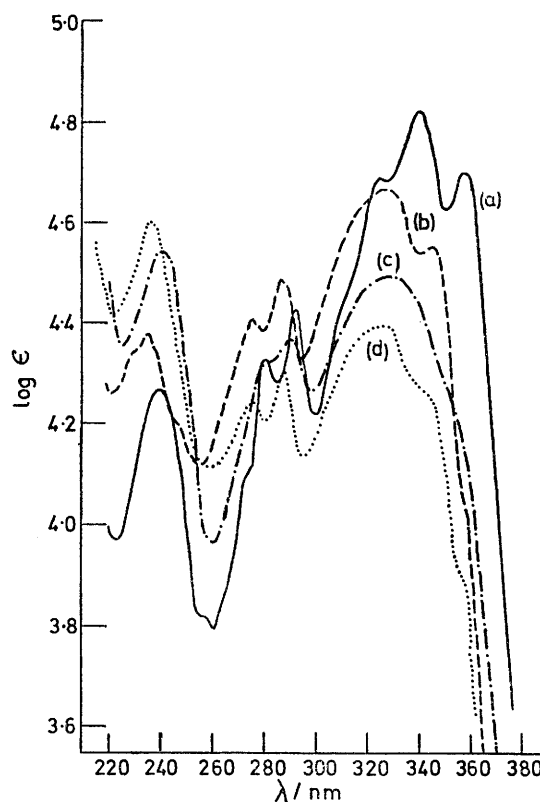

FIGURE 1   U.v. spectra (MeOH) of (a) *trans, trans*-1-(β-naphthyl)-4-phenylbutadiene;   (b)   *trans*-1-(β-naphthyl)-4-phenylbutenyne;   (c) the *cis,trans*-butadiene isomer;   (d) the *cis*-butenyne isomer

spectrum of (23a) is completely temperature independent. It is not surprising that a similar conclusion can be

[9] W. H. Laarhoven and P. G. F. Boumans, *Rec. Trav. chim.*, 1975, **94**, 114.

drawn for the 1-(3-phenanthryl)butenynes (18a) and (19a).

The butenyne (24), in which the olefinic protons have been replaced by a bulky tetramethylene bridge, does not show the low-field absorption for H-2 which is observed in other cis-1-(1-naphthyl)butenynes [e.g. (8a) and (10a)]; this can be ascribed to a deshielding influence of the acetylene group. One explanation may be that the average plane of the cyclohexene ring is perpendicular to the plane of the naphthyl group in this compound.

ascribed to the shorter length of the triple bond and the higher electronegativity of acetylenic carbon atoms.

As expected, the A band at the long-wavelength side of a cis-butenyne is always found at a shorter wavelength and has a lower molar extinction than that of the corresponding trans-isomer. Such hypo- and hypso-chromic shifts increase with increasing deviation from coplanarity as is indicated by the u.v. spectra of the compounds (10a), (13a), and (24) (see Figure 2). In (24) the A band is reduced to a slight inflection; the remaining maxima

TABLE 3

U.v. spectra of 1,4-diarylbutenynes

Compound	λ_{max}/nm (MeOH) (log ε) †
(1a)	213 (4.57), [235 (4.17)], 243 (4.24), 259 (4.50), 268 (4.53), 288 (4.15), 298 (4.34), 311 (4.34), [323 (3.72)], [332 (3.32)], 350 (2.95)
(1b)	212 (4.29), [230 (4.13)], 236 (4.29), 244 (4.37), 261 (4.57), 270 (4.61), 286 (4.13), 297 (4.49), 311 (4.52), [325 (3.70)], 334 (3.50), 351 (3.10)
(2a)	214 (4.50), [222 (4.33)], 235 (4.26), 243 (4.28), [253 (4.31)], 261 (4.44), 271 (4.46), 287 (4.19), 299 (4.36), 313 (4.37), [325 (3.71)], [332 (3.46)], 350 (2.89)
(2b)	[230 (4.18)], 237 (4.32), 245 (4.39), [254 (4.41)], 262 (4.58), 272 (4.62), 287 (4.36), 298 (4.57), 313 (4.60), [333 (3.65)], 351 (3.09)
(3a)	[230 (4.51)], 236 (4.61), 275 (4.24), 287 (4.31), [295 (4.13)], 325 (4.40), 340 (4.27), [356 (3.90)]
(3b)	[232 (4.39)], 236 (4.43), 247 (4.36), [256 (4.40)], [265 (4.51)], 275 (4.60), 286 (4.62), [317 (4.63)], 325 (4.67), 345 (4.55), [357 (4.05)]
(4) *	266 (4.27), 276 (4.34), 291 (4.20), 299 (4.24), 354 (4.63), [350 (4.62)], 374 (4.55)
(5a)	238 (4.56), 276 (4.21), 287 (4.26), [321 (4.37)], 327 (4.39), [342 (4.27)], [356 (3.98)]
(5b)	237 (4.38), 276 (4.37), 287 (4.44), 327 (4.66), 347 (4.54), [320 (4.62)]
(6)	[220 (4.43)], 238 (4.43), [259 (4.38)], 282 (4.60), [287 (4.60)], 292 (4.61), 332 (4.61), [348 (4.49)]
(7a)	239 (4.58), [282 (4.18)], 295 (4.26), 323 (4.44), [345 (4.21)]
(7b)	235 (4.32), 256 (4.17), 281 (4.47), 291 (4.50), 330 (4.64), [350 (4.45)]
(8a)	228 (4.54), 270 (4.22), 279 (4.29), 328 (4.20)
(8b)	233 (4.52), 274 (4.10), 281 (4.16), 331 (4.46)
(9) *	[267 (3.83)], 352 (4.48)
(10a)	233 (4.54), 273 (4.23), 282 (4.30), 335 (4.21)
(10b)	236 (4.55), [275 (4.25)], 282 (4.28), 336 (4.49)
(11)	236 (4.50), [277 (4.04)], 283 (4.04), 336 (4.49)
(12)	238 (4.45), [281 (4.12)], 286 (4.13), 351 (4.50)
(13a)	224 (4.65), [268 (4.27)], 275 (4.33), [289 (4.16)], [325 (3.83)]
(13b)	225 (4.70), 277 (4.26), 311 (4.31)
(14)	223 (4.23), [227 (4.20)], [248 (4.01)], [303 (4.57)], 312 (4.59), [331 (4.42)]
(15) *	[268 (3.94)], 277 (4.07), 287 (4.16), [325 (4.41)], 340 (4.51), 363 (4.41)
(16)	225 (4.22), [231 (4.19)], [249 (4.06)], [312 (4.56)], 324 (4.61), [345 (4.42)]
(17)	236 (4.26), [241 (4.23)], 316 (4.36), 335 (4.19)
(18a)	238 (4.60), 245 (4.62), 252 (4.68), 272 (4.41), 283 (4.36), [328 (4.39)], 339 (4.44), [349 (4.33)], [360 (4.23)], [367 (4.00)]
(18b)	[226 (4.37)], [241 (4.45)], 248 (4.49), 252 (4.57), 274 (4.47), 285 (4.46), [331 (4.64)], 341 (4.70), [352 (4.57)], [368 (4.24)]
(19a)	246 (4.65), 252 (4.68), 273 (4.38), 284 (4.33), [331 (4.33)], 340 (4.37), [349 (4.30)], [360 (4.19)]
(19b)	244 (4.49), 252 (4.56), 274 (4.44), 285 (4.44), 342 (4.72), [360 (4.55)], [368 (4.33)]
(20)	222 (4.64), [250 (4.50)], 260 (4.57), 286 (4.58), 341 (4.43)
(21)	[227 (4.61)], [252 (4.48)], 260 (4.54), 280 (4.54), 289 (4.56), 342 (4.45)
(22a)	245.5 (4.69), 254 (4.76), 276.5 (4.43), 288 (4.39), [332 (4.36)], 345 (4.42), [363 (4.25)]
(22b)	248 (4.54), 254 (4.60), 279 (4.50), 290 (4.50), 334 (4.61), 347 (4.70), [365 (4.55)]
(23b)	218 (4.47), 235 (4.44), 249 (4.43), 274 (4.57), 311 (4.65), [319 (4.61)], 347 (4.59)
(24)	222 (4.86), [258 (4.18)], 277 (4.39), 296 (4.26)

* Measured in CH_2Cl_2. † Square brackets refer to inflections.

U.v. Spectra.—The u.v. spectra of cis- and trans-butenynes are of the same form as those of similarly substituted cis,trans- and trans,trans-butadienes (see Figure 1). The absorption maxima are, however, at slightly shorter wavelengths, and the extinction coefficients are always lower for the butenynes. These differences are generally found when a double bond in a polyene system is replaced by a triple bond;[10] they are

agree with those of a summed spectrum of the two chromophoric systems: 1-methylnaphthalene,[11] λ_{max}. 224 (ε 50 000), 271 (5 200), 281 (6 000), 291 (4 000), 312 (340), and 317 nm (160); and 1-phenylbutenyne,[12] λ_{max}. 220 (ε 15 000) and 276 nm (15 600). Apparently conjugation between these systems is completely lost in this compound. In (7) the influence of steric hindrance is much less extreme, since in the u.v. spectrum of this

[10] A. E. Gillam, E. S. Stern, and E. R. H. Jones, in ' An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry,' Edward Arnold, London, 1962, p. 100, and references cited therein. See also G. Berthier and B. Pullman, Compt. Rend., 1949, 228, 397.

[11] DMS UV Atlas, E1/19.
[12] Though the spectrum of 4-phenylbutenyne is not known, it may be assumed to be similar to that of 1-phenylbutenyne, see N. B. Kupletskaya, A. V. Dombrovsky and A. P. Terent'ev, J. Gen. Chem. (U.S.S.R.), 1957, 27, 3070.

compound by comparison with that of (3) only the fine structure of the A band has disappeared.

Mass Spectra.—The mass spectra of the unsubstituted 1,4-diarylbutenynes show a characteristic pattern. From the molecular ion, which is in most cases the base
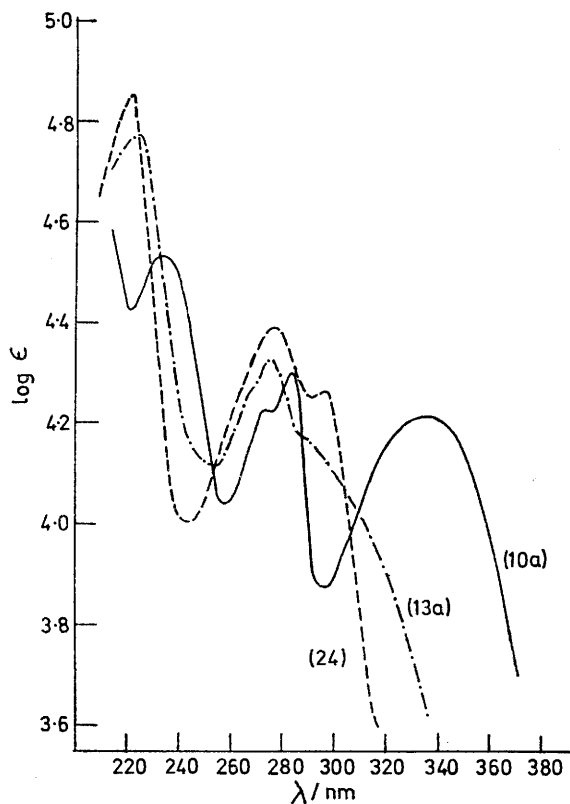

FIGURE 2 U.v. spectra (MeOH) of *cis*-diarylbutenynes (10a) (13a), and (24)

peak, two hydrogen atoms are eliminated ($M^+ - 1$, 70—90%; $M^+ - 2$, 60—80%). The abundance of the M^+ − 1 peak always exceeds that of $M^+ - 2$. If the 1-aryl groups are large as in (18) and (23) abundant peaks are present at $M^+ - 77$ and $M^+ - 78$. This is due to the loss of the phenyl group at C-4 as can be concluded from the peaks at $M^+ - 105$ and $M^+ - 106$ (dimethylphenyl groups) in the spectra of (19), (21), and (23).

In all cases an $M^+ - 15$ (5—10%) fragment is present but in lower abundance than in stilbenes (40%) and 1,4-diarylbutadienes (26%).[13]

In methyl-substituted compounds the $M^+ - 15$ peaks dominate, $M^+ - 1$ is reduced, and $M^+ - 2$ is absent or very small. In the compounds with other substituents in the 1-aryl group the characteristic fragmentation of these groups is found. The $M^+ - 1$ and $M^+ - 2$ peaks are then absent.

[13] R. A. W. Johnstone and S. D. J. Ward, *J. Chem. Soc. (C)*, 1968, 2540.
[14] J. C. Sheenan and F. R. Gilmont, *Org. Synth.*, 1963, Coll. Vol. IV, 813.
[15] L. Crombie, S. H. Harper, and R. J. D. Smith, *J. Chem. Soc.*, 1957, 2758.

EXPERIMENTAL

M.p.s were determined with a Leitz m.p. microscope and are uncorrected. U.v. spectra were measured with a Cary 15 or a Beckman DK2A spectrophotometer, mass spectra with a Varian MAT SM2B mass spectrometer, and n.m.r. spectra with a Varian T60, HA100, or XL100 spectrometer for 4—10% solutions in CS_2 with tetramethylsilane as an internal, or hexamethyldisilane as an external, reference. The n.m.r. spectra are concentration independent. N.m.r. frequencies were determined by the side-band technique. Peak assignments were done by spin decoupling or tickling and by comparison with spectra of known compounds.

Chromatographic separations were done by column chromatography on aluminium oxide (Merck; activity 1; neutral) or silica gel (Merck; 0.05—0.2 mm). G.l.c. analyses were done with a Varian Aerograph 1200 gas chromatograph (SE30 column) supplied with a flame ionisation detector.

Propiolaldehydes.—The syntheses of propynal,[14] but-2-ynal,[15] and phenylpropiolaldehyde [16,17] have been described.

3,5-Dimethylphenylpropiolaldehyde. A solution of methyllithium (16.7 g of lithium and 146.0 g of methyl iodide) in absolute ether was dropped into a suspension of 3,5-dimethylbenzoic acid (45 g) in dry ether (200 ml) and the mixture was stirred vigorously to dissolve the precipitated lithium salt of the acid. After 4 h the solution was poured into ice–water. The organic layer was washed with water until neutral and dried ($MgSO_4$). Evaporation of the solvent yielded 3′,5′-dimethylacetophenone (40.5 g, 91%), b.p. 78° at 1.5 mmHg. A solution of the ketone (45.7 g) in benzene (100 ml) was dropped into a solution of phosphorus pentachloride (71 g) in the same solvent (100 ml) at 60—70°. The mixture was refluxed for 4 h, then poured into ice–water, and extracted with benzene. The combined extracts were washed with 5% sodium hydrogen carbonate solution and water until neutral and dried ($MgSO_4$). Evaporation of the solvent and distillation yielded 1-chloro-1-(3,5-dimethylphenyl)ethylene (35.5 g, 69%), b.p. 107—109° at 16 mmHg. A solution of this vinyl chloride (35.5 g) in dry ether (75 ml) was slowly added to a solution of sodium amide in liquid ammonia [27.5 g of sodium, 0.25 g of iron(III) nitrate, ca. 250 ml of ammonia]. The mixture was stirred for 3 h at −70° and then neutralized with ammonium chloride. The solvent was evaporated and the residue was washed with water and extracted with ether. The ethereal extract was washed with water until neutral, dried ($MgSO_4$), and evaporated. Distillation of the residue over a spinning band column yielded 3,5-dimethylphenylacetylene (20 g, 72%), b.p. 75—77° at 14 mmHg. The acetylene was converted into the desired aldehyde *via* the corresponding diethyl acetal as described for phenylpropiolaldehyde.[16,17] 3,5-Dimethylphenylpropiolaldehyde diethyl acetal was obtained in 58% yield, b.p. 119° at 0.5 mmHg, δ(CCl_4) 1.23 (6 H, t, $2CH_3$), 2.26 (6 H, s, $2CH_3$), 3.57 (2 H, q, CH_2), 3.66 (2 H, q, CH_2), 5.29 (1 H, s, CH), 6.82 (1 H, s), and 6.99 (2 H, s). Acid hydrolysis gave 3,5-dimethylphenylpropiolaldehyde in 90% yield, b.p. 111° at 2.5 mmHg, δ(CCl_4) 2.30 (6 H, s, $2CH_3$), 7.03 (1 H, s), 7.14 (2 H, s), and 9.31 (1 H, s, CHO).

α-Naphthylpropiolaldehyde. Starting with α-naphthylacetylene [18] the above procedure for the introduction of the

[16] C. F. H. Allen and C. O. Edens, jun., *Org. Synth.*, 1965, Coll. Vol. III, 731.
[17] B. W. Howk and J. C. Sauer, *J. Amer. Chem. Soc.*, 1958, **80**, 4607.
[18] K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1970, **43**, 3567.

formyl group was used. The intermediate diethyl acetal was obtained in 55% yield, b.p. 150—152° at 0.8 mmHg, $\delta(CCl_4)$ 1.23 (6 H, t, 2CH$_3$), 3.68 (2 H, q, CH$_2$), 3.78 (2 H, q, CH$_2$), 5.49 (1 H, s, CH), 7.19—8.00 (6 H, m), and 8.30 (1 H, m, α-H). Hydrolysis gave the desired aldehyde as an oil which was purified by column chromatography over silica gel and elution with benzene–pentane (1 : 1), $\delta(CCl_4)$ 7.03—7.86 (6 H, m), 8.14 (1 H, m, α-H), and 9.39 (1 H, s, CHO).

Arylmethyl Halides and Arylmethyltriphenylphosphonium Halides.—Most of these compounds have been described previously (see Table 4). New arylmethyl bromides were made using a general procedure which consisted of heating a solution of the appropriate methyl-substituted aromatic compound in carbon tetrachloride with N-bromosuccinimide

methoxide (0.04 mol) in methanol (20 ml) was added to a solution of an arylmethyltriphenylphosphonium halide (0.02 mol) and propargylaldehyde (0.02 mol) in methanol or dimethylformamide (80 ml) with stirring. In methanol, part of the butenyne formed could be filtered off after 16 h as a *cis–trans*-mixture. The filtrate, or with dimethylformamide as solvent, the reaction mixture, was evaporated. For the separation of the *cis–trans*-mixture water was added and the suspension was extracted with benzene. The extracts were washed with water, dried (MgSO$_4$), evaporated, and the remaining oil separated by column chromatography over silica gel. Successive elutions with hexane, hexane–benzene (9 : 1), and hexane–benzene (3 : 1) subsequently gave the changed alkylaromatic compound, the *cis*-, and the *trans*-product. The isomers were further purified by repeated

TABLE 4

M.p.s of arylmethyl halides and arylmethyltriphenylphosphonium halides

| Ar | ArCH$_2$Br | | ArCH$_2$P$^+$(Ph)$_3$Br$^-$ | |
	M.p. or b.p. [p/mmHg] (°C)	Reference	M.p. (°C)	Reference
Phenyl			285—290	277—279 [a]
p-Methoxyphenyl	106(2.5)	104(1.5) [b]	236—238	236—238 [c]
3,5-Dimethylphenyl	39	40 [d]	317—321	
1-Naphthyl	118(0.6)	175(10) [e]	286—288	
2-Naphthyl	56	56 [j]	247—248	248—251 [g]
2-Methyl-1-naphthyl [h]	61—63	62—64 [i]	283—285	
4-Methyl-1-naphthyl	84—85	85 [k]	238—241	
4-Carboxymethyl-1-naphthyl			220—232	
1-Bromo-2-naphthyl	106—108	107—108 [m]	228—248	
8-Phenyl-2-naphthyl [n]			278—281	
3-Phenanthryl [o]	116—117	117.5 [p]	295—298	291—292 [q]
1-Phenyl-9-phenanthryl [p]	140—141		257—261	
1-(3,5-Dimethylphenyl)-9-phenanthryl	172—174			
5,7-Dimethyl-3-phenanthryl	100—102	100—102 [t]		
2-Benzo[c]phenanthryl			320—321	320—321 [s]

[a] G. Wittig and W. Haag, *Chem. Ber.*, 1955, **88**, 1654. [b] J. W. Baker, *J. Chem. Soc.*, 1932, 2631. [c] A. W. Johnson and V. L. Kyllingstad, *J. Org. Chem.*, 1966, **31**, 334. [d] M. Weiler, *Chem. Ber.*, 1900, **33**, 339. [e] N. P. Buu-Hoï and J. Lecocq, *J. Chem. Soc.*, 1946, 830. [f] N. P. Buu-Hoï, *Annalen*, 1944, **556**, 1. [g] J. P. Geerts and R. H. Martin, *Bull. Soc. chim. belges.*, 1960, **69**, 563. [h] Chloride instead of bromides. [i] R. T. Arnold, J. S. Buckley, jun., and J. Richter, *J. Amer. Chem. Soc.*, 1947, **69**, 2322. [k] G. Lock and R. Schneider, *Chem. Ber.*, 1958, **91**, 1770. [l] 1-Carboxymethyl-4-methylnaphthalene, F. Mayer and A. Sieglitz, *Ber.*, 1922, **55**, 1835. [m] M. S. Newman and A. I. Kosak, *J. Org. Chem.*, 1949, **14**, 375. [n] 7-Methyl-1-phenylnaphthalene, J. Bonnier and J. Rinaudo, *Bull. Soc. chim. France*, 1970, **37**, 146. [o] 3-Methylphenanthrene, C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373. [p] W. E. Bachmann and M. C. Kloetzel, *J. Amer. Chem. Soc.*, 1937, **59**, 2207. [q] S. Akiyama, N. Nakasuji, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1971, **44**, 2231. [r] The synthesis of 9-methyl-1-phenylphenanthrene by photocyclisation of 1-(4-methyl-1-naphthyl)-4-phenylbutenyne is described in a subsequent paper. [s] W. H. Laarhoven and R. G. M Veldhuis, *Tetrahedron*, 1972, **28**, 1811. [t] A. H. A. Tinnemans and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1974, **96**, 4611.

in the presence of dibenzoyl peroxide under illumination. Yields were between 70 and 90%. For the conversion into a triphenylphosphonium halide the bromomethyl aromatic compound (0.01 mol), with or without purification, and triphenylphosphine (0.01 mol) were dissolved in xylene (200 ml) and refluxed for 4 h. After cooling the precipitate was filtered, washed with hexane or absolute ether, and dried. It was employed in a Wittig synthesis without further purification.

9-Bromomethyl-1-(3,5-dimethylphenyl)phenanthrene. Irradiation of a solution of 1-(4-hydroxymethyl-1-naphthyl)-4-phenylbutenyne yielded 1-(3,5-dimethylphenyl)-9-hydroxymethylphenanthrene.* The product was dissolved in benzene, and the solution saturated with hydrogen bromide. After 20 h the mixture was extracted with 5% sodium hydrogen carbonate solution and water until neutral, dried (MgSO$_4$), and evaporated. The oily residue crystallised from carbon tetrachloride, yield 93%, m.p. 172—174 °C.

1,4-Diarylbut-1-en-3-ynes.—Most of the butenynes were obtained *via* the following general procedure. Sodium

* Syntheses and physical constants are given in ref. 2.

column chromatography over aluminium oxide and elution with the same solvent mixtures, followed by crystallisation from methanol.

Only with (2-methyl-1-naphthylmethyl)triphenylphosphonium chloride was a stronger base (potassium t-butoxide in dimethylformamide, or n-butyl-lithium in dry ether) necessary for the Wittig reaction. Physical data of the products are given in Tables 1—3.

trans-4-(3,5-Dimethylphenyl)-1-(4-hydroxymethyl-1-naphthyl)but-1-en-3-yne (11).—This compound was obtained by reduction of the corresponding methoxycarbonylnaphthyl derivative with LiAlH$_4$ as described for the preparation of 6-bromomethyl-2,4-dimethylphenanthrene. It was formed in 83% yield, m.p. 133—134.5° (from methanol) (see Tables 1—3).

1-(1-Naphthyl)-2-phenylethynylcyclohexene (24).—2-(1-Naphthyl)cyclohexanone was prepared by slow addition of 2-chlorocyclohexanone [19] (0.21 mol) in dry ether (75 ml) to 1-naphthylmagnesium bromide [obtained from magnesium

[19] M. S. Newman, M. D. Farbman, and H. Hipscher, ref. 16, p. 188.

(0.21 mol) and 1-bromonaphthalene (0.21 mol) in ether] as described by Newman [20] for 2-phenylcyclohexanone. Distillation gave the crude ketone, which crystallised on addition of methanol–light petroleum (60—80°), yield 62%, m.p. 82—83°, b.p. 164—168° at 0.6 mmHg, δ(CCl$_4$) 1.78—2.78 (8 H, m), 4.26—4.50 (1 H, m), 7.34—7.68 (4 H, m), and 7.70—8.04 (3 H, m). A solution of phenyl-lithium [bromobenzene (13.7 g), lithium (1.25 g) in 100 ml of dry ether] was added to a well stirred solution of phenylacetylene (8.2 g) in dry ether (75 ml). The solution was refluxed for 1 h, then a solution of 2-(1-naphthyl)cyclohexanone (16.3 g) in dry ether (200 ml) was added, and the solution was heated again for 3 h. After cooling, water was added, the mixture was neutralised with dilute hydrochloric acid, and extracted with ether. The extract was dried and evaporated, and the remaining crude alcohol shaken with 90% formic acid for 24 h. After evaporation of the mixture, addition of water, and extraction with benzene, the extract was washed with 5% sodium hydrogen carbonate solution and water, dried, and subjected to column chromatography over aluminium oxide. The desired product was eluted with pentane–benzene (16 : 1), and crystallised from methanol, m.p. 75—77° (see Tables 1—3).

[20] M. S. Newman and M. D. Farbman, *J. Amer. Chem. Soc.*, 1944, **66**, 1550.