Tetrahedron Letters No.38, pp. 3373-3382, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE PHOTO-ADDITION OF TOLAN TO SOME NAPHTHALENES: THE FORMATION OF DERIVATIVES OF 2,3-BENZOTETRACYCLO$[3.2.1.0^{5,7}.0^{6,8}]$OCTENE-2

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(Received 29 July 1965)

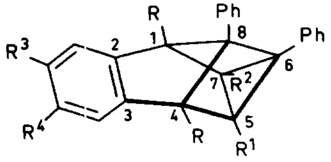
THE light-induced addition of certain acetylenes to benzene is well known (1,2,3) but to our knowledge such reactions have not previously been observed with naphthalenes. It has now been found that irradiation of a solution of naphthalene and tolan in cyclohexane with a Pyrex-jacketed Philips laboratory burner (HPK 125W) gives as main product (29% after 120 hours; based on tolan) a hydrocarbon, $C_{24}H_{18}$ (4), m.p. 133-134°, for which the structure (I) is proposed. Tolan has been added similarly to 1,4-dimethylnaphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, and 2,7-dimethylnaphthalene to give appreciably better yields of the adducts (II), (III), (IV), and (V), respectively (see Table 1). Under the conditions used 1,4-dimethylnaphthalene

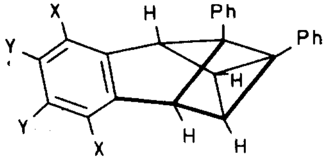
TABLE 1

Photo-Addition of Tolan to Some Naphthalenes at 30-35°: Yields of the Adducts (I)-(V)

Adduct	I	I	II	III	IV	V
Starting materials (in mmole)						
Tolan	10	40	6.4	6.4	12.8	6.4
Naphthalene	40	120	25.6	25.6	51.2	25.6
Volume of cyclohexane (ml)	250	370	50	50	250	50
Time of irradiation (hours)	70	120	77	72	96	73
Yield (% based on tolan)	23	29	57	58	44	45
Melting point (°C)	133-134	133-134	152	147	99	139

and 2,3-dimethylnaphthalene react with tolan preferentially at the methyl-substituted rings, and so far the isomeric adducts (VI) and (VII) have not been isolated.





(I): $R=R^1=R^2=R^3=R^4=H$;

(II): $R=Me$; $R^1=R^2=R^3=R^4=H$;

(III): $R^1=R^2=Me$: $R=R^3=R^4=H$;

(IV): $R^1=R^3=Me$; $R=R^2=R^4=H$;

(V): $R^1=R^4=Me$: $R=R^2=R^3=H$;

(VI): X=Me; Y=H;

(VII): X=H; Y=Me.

The mass spectrum (5) of the parent compound established the molecular weight as 306. Other relatively intense peaks occurred at m/e 178 (tolan) and 128 (napthalene), indicating that the photo-addition did not involve rearrangements of the carbon skeletons of the components. The ultraviolet spectrum (Table 2) ruled out the presence of a stilbene-like arrangement of two of the

TABLE 2

Ultraviolet Absorption of the Adducts (I)-(V)*

	Maxima	Points of Inflexion	Shoulders
I	274 (2,300)	235 (13,000)	225 (19,000)
II	275 (3,490)	266 (5,780)	225 (20,700)
III	280 (3,090)	252 (10,500)	230 (17,400)
IV	275 (2,850)	256 (9,400)	240 (13,400)
V	280 (3,800)	255 (12,600)	225 (25,000)

* Measured in 95% ethanol; expressed as molecular extinction coefficients.

benzene rings in the adduct. Its saturated character was demonstrated when the naphthalene-tolan adduct was recovered quantitatively after treatment with excess potassium permanganate in boiling acetone for 40 hours. Exhaustive oxidation with chromic trioxide in glacial acetic acid at 75° gave benzoic acid and phthalic acid, identified by paper chromatography and gas chromatography (methyl esters); other acids were not detected. Provided that rearrangements altering the number of substituents linked to the aromatic rings do not precede the oxidation, these findings indicate that only one of the rings of naphthalene takes part in the photo-addition and that the phenyl groups originally present in tolan are still present as such in the adduct. This conclusion is supported by the areas of the signals in the p.m.r. spectrum (6) of the adduct, which consists of a multiplet between ca. 6.8 and 7.2 p.p.m. (14 protons) and two quartets (2 protons each), which are centred at 4.24 and 2.52 p.p.m. respectively, and exhibit splittings of 0.3 and 1.4 c/s (measured from the centre of each quartet). A feature of this spectrum is the symmetry of the non-aromatic protons, which is reflected in the A_2X_2 pattern. The infrared spectrum provided further evidence for the presence of mono-substituted benzene rings, as the two most intense bands occurred at 695 and 745 cm^{-1} (7); other strong bands occurred inter alia at 2975, 1135, 1020, 935, and 860 cm^{-1}. Absorption at or near these frequencies has been observed in the infrared spectra of cyclobutanes (8,9,10) and cyclopropanes (8,11).

The possibility that a cyclopropane ring was formed during the photo-addition received support when it was found that in the presence of 5% palladium-on-carbon and at atmospheric pressure and room temperature the naphthalene-tolan adduct took up one mole of hydrogen to form a liquid dihydro-derivative (VIII) in yields exceeding 90% (gas chromatography). This reaction was accompanied by minor changes in the ultraviolet spectrum, while the p.m.r.

spectrum showed that the six non-aromatic protons in (VIII) were non-equivalent (Fig. 1).

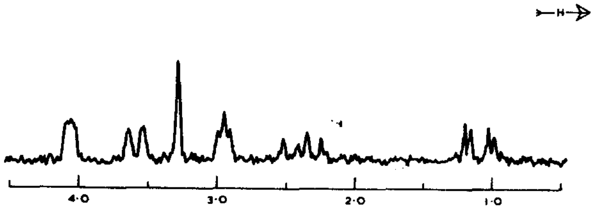
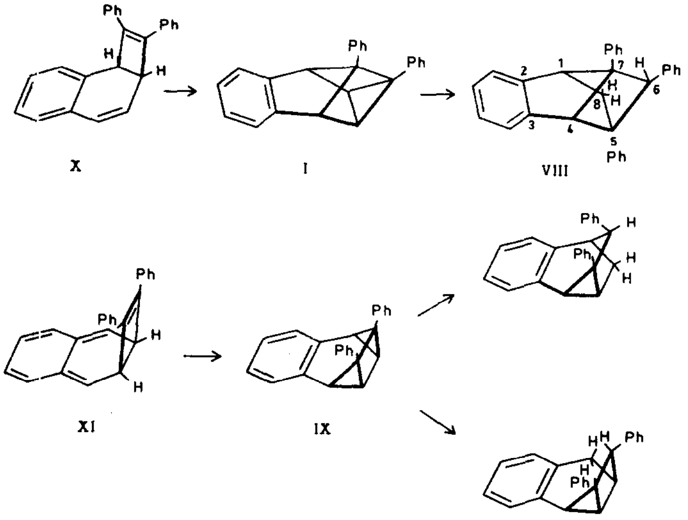


FIG. 1
Part of the p.m.r. spectrum of (VIII).

The evidence presented so far prompted close scrutiny of two possible structures, (I) and (IX), for the naphthalene-tolan adduct. Formally, these two structures could be derived from two different "primary" adducts, (X) and (XI) (shown as <u>endo</u>-isomers), which in turn could be formed from naphthalene by 1,2-addition or by 2,3-addition respectively:



X

I

VIII

XI

IX

A distinction between these structures in favour of (I) was suggested by the observation that the dihydro-derivative of the adduct did not react further with hydrogen-palladium, even under forcing conditions. The structures (I) and (IX) both contain carbon-carbon bonds which are at the same time situated in a cyclopropane ring and in a benzylic position relative to a phenyl group, and hydrogenolysis of one of these bonds in either (I) or (IX) would yield dihydro-derivatives with six non-equivalent (non-aromatic) protons. However, while the dihydro-compound (VIII), which is derived from (I), should not react any further, each of the possible dihydro-derivatives of (IX) contains another benzylic bond that is incorporated in a cyclopropane ring, and should thus be susceptible to further hydrogenolysis.

Decisive evidence in favour of structure (I) for the naphthalene-tolan adduct came from further analysis of the p.m.r. spectrum of the dihydro-derivative (Fig. 1). This spectrum was consistent only with structure (VIII), provided that the stereoisomer was chosen, which was formed by cis-addition of hydrogen to either of the benzylic bonds in the cyclopropane ring of (I). The assignments proposed (Table 3) are based largely on the magnitude of the coupling constants, which correlate with the dihedral angles as postulated by Karplus (12,13). These angles vary in (VIII) from ca. 30° to 90°, as measured on Dreiding models, and the coupling constants lie between 6.3 and 0 c/s approximately. The gem-coupling of 10.5 c/s between the methylene protons at the 8-position lies below the usual range (14), but low gem-coupling constants are common in small rings (15,16,17). The assignments proposed for the p.m.r. spectrum of (VIII) are confirmed by the spectra of the dihydro-derivatives (XII) and (XIII) of the methyl-substituted adducts (II) and (IV), described below (see also Table 3).

TABLE 3

n.m.r. Spectra (6) of the Adducts (I)-(V), and of (VIII), (XII) and (XIII)*

(I)

Shift:	_ca._ 7	4.24	2.52
No. of protons:	14	2	2
Multiplicity:	m	dd	dd
Assignments:	Ar	1-,4-	5-,7-

Coupling constants: $J_{1,7} + J_{1,5} = 2.8$

(II)

Shift:	6.9-7.4	6.4-6.6	2.40	1.68
No. of protons:	12	2	2	6
Multiplicity:	m	m	s	s
Assignments:	Ar	Ar	5-,7-	Me

(III)

Shift:	ca. 7.1	3.99	1.31
No. of protons:	14	2	6
Multiplicity:	m	s	s
Assignments:	Ar	1-,4-	Me

(IV)

Shift:	ca. 7	4.12	4.00	2.28	2.23	1.29
No. of protons:	13	1	1	3	1	3
Multiplicity:	m	d	s	s	d	s
Assignments:	Ar	1	4	Ar-Me	7-	Me-

Coupling constants: $J_{1,7} = 2.6$; $J_{1,4} \sim 0$; $J_{4,7} \sim 0$.

(V)

Shift:	ca. 7	4.12	3.99	2.33	2.26	1.31
No. of protons:	13	1	1	3	1	3
Multiplicity	m	d	s	s	d	s
Assignments	Ar	1-	4-	Ar-Me	7-	Me

Coupling constants: $J_{1,7} = 2.6$; $J_{1,4} \sim 0$; $J_{4,7} \sim 0$.

(VIII)

Shift:	ca. 7	4.08	3.60	3.29	2.94	2.38	1.09
No. of protons:	14	1	1	1	1	1	1
Multiplicity:	m	m	d	s	dd	dd	dd
Assignments:	Ar	4-	1-	6-	5-	8x-	8n-

Coupling constants: $J_{1,4} \sim 1$; $J_{1,8n} \sim 0$; $J_{1,8x} = 6.3$; $J_{4,5} = 2.6$; $J_{5,6} \sim 0$;
$J_{5,8n} = 2.6$; $J_{5,8x} \sim 0$; $J_{8n,8x} = 10.5$

(XII)

Shift:	ca. 7.1	6.6-6.8	3.57	2.69	2.01	1.50	1.28	1.27
No. of protons:	12	2	1	1	1	3	3	1
Multiplicity:	m	m	s	d	d	s	s	dd
Assignments:	Ar	Ar	6-	5-	8x-	1-Me	4-Me	8n-

Coupling constants: $J_{5,6} \sim 0$; $J_{5,8n} = 2.3$; $J_{5,8x} \sim 0$; $J_{8n,8x} = 10.3$

(XIII)

Shift:	ca. 7	3.80	3.41	3.29	2.26	2.23	0.99	0.93
No. of protons:	13	1	1	1	1	3	3	1
Multiplicity:	m	s	s	d	dd	s	s	d
Assignments:	Ar	4-	6-	1-	8x	Ar-Me	Me	8n

Coupling constants: $J_{1,8n} \sim 0$; $J_{1,8x} = 6.5$; $J_{8n,8x} = 10.5$

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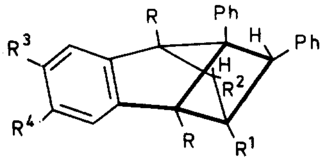
* Chemical-shift data are given in p.p.m. relative to TMS=0 as internal standard. Coupling constants are given in c/s. Abbreviations used are as follows: m, multiplet; s, singlet; d, doublet; dd, doubletof doublet; n, _endo_; x, _exo_.

The chemical-shift positions of the non-aromatic protons in (I) are of interest as both quartets absorb at lower frequencies than protons in typically benzylic positions or in phenylcyclopropane (18,19). Inspection of Prentice-Hall "framework molecular models" shows that, except for rotation of the phenyl groups, the structure (I) is entirely rigid and the 1- and 4-protons are situated in planes that are almost coplanar with the adjacent aromatic ring. Moreover, the most favoured conformations of the phenyl substituents at the 6- and 8-positions are those in which these groups exert their deshielding influence on the 1-,4-,5-, and 7-protons. Using the chemical-shift position (3.35 p.p.m.) of the bridgehead protons in benzonorbornene (20), the deshielding effect due to the 6- and 8-phenyl groups experienced by the 1- and 4-protons in (I) was estimated (21) to be about 0.7 p.p.m., in satisfactory agreement with the observed chemical shift of 4.24 p.p.m.

The structure (I) now proposed for the naphthalene-tolan adduct is confirmed by spectral and chemical properties of the dimethyl derivatives (II), (III), (IV), and (V), which are formed by photo-addition of tolan to 1,4-, 2,3-, 2,6-, and 2,7-dimethylnaphthalene. Thus, the ultraviolet spectra of these compounds resemble closely that of the parent compound (I) (Table 2), and relatively strong peaks occur in the mass spectrum of each dimethyl-derivative at m/e 178 (tolan) and 156 (dimethylnaphthalene). The p.m.r. spectra of the dimethyl-adducts (II)-(V) and of (I) are mutually consistent (Table 3), except for the appearance of two discrete multiplets between 7.5 and 6.95 p.p.m. (12 protons) and between 6.6 and 6.4 p.p.m. (2 protons) in the spectrum of (II). However, inspection of molecular models shows that the methyl groups at the 1- and 4-positions interfere strongly with the free rotation of the 8-phenyl group. In the most favourable conformation of this group its 2- and 6-protons are exposed to the shielding effects of the 6-phenyl group and of the adjacent benzene ring.

Further support for the structure (VIII) proposed for the dihydro-derivative of the naphthalene-tolan adduct (I) was obtained from the p.m.r. spectra of the compounds (XII) and (XIII) resulting from hydrogenolysis of the adducts (II) and (IV). The fact that (IV) gave the dihydro-compound (XIII) rather than the isomer (XIV) indicated that hydrogenolysis of the cyclopropane ring had occurred preferentially at the least-substituted benzylic bond. In this context the resistance of the 2,3-dimethylnaphthalene-tolan adduct (III) towards hydrogenolysis, even under forcing conditions (55°), is of interest because in this compound the cyclopropane ring is hexa-substituted. Steric factors hindering approach of the cyclopropane ring to the catalyst would explain these observations.



(XII): R=Me; $R^1=R^2=R^3=H$; $R^4=H$.

(XIII): $R^1=R^3=Me$; $R^2=R=H$; $R^4=H$.

(XIV): $R=R^1=R^3=H$; $R^2=R^4=Me$.

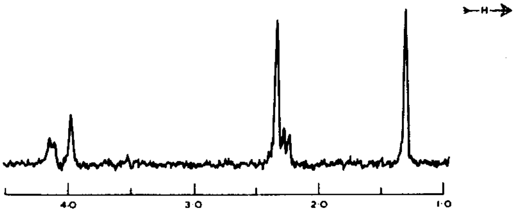


FIG. 2
Part of the p.m.r. spectrum of the adduct (V).

The p.m.r. spectra of the adducts (IV) and (V) (Fig. 2) yielded the coupling constants between 1- and 4-protons (approx. 0 c/s) and between 1- and 7-protons (2.6 c/s). With these constants the A_2X_2 part of the spectrum of (I) was analysed. With J_{AX} = 2.6 c/s and $J_{AA'}$ = 0, or $J_{AA'}$ = 1 c/s, $J_{XX'}$ was varied. Good agreement with the observed spectrum was obtained with $J_{XX'}$ in the range 6-8 c/s. In particular, the outermost lines of the A_2X_2 system (cf. Ref. 22) assumed intensities which were probably too small for detection. A value between 6 and 8 c/s for $J_{XX'}$ agrees with cis-coupling constants observed in cyclopropanes (16).

The scope of the new reaction and the chemistry of the adducts are being studied currently.

Acknowledgments. - We thank Dr. J.S. Shannon for the determination and interpretation of mass spectra, Dr. J.R. Wilmshurst for experiments involving analytical and preparative gas chromatography, and Miss P.E. Rosevear for ultraviolet spectra.

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