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MEDIUM-SIZED CYCLOPHANES—VIII

DI-, TETRA- AND HEXAMETHYL[2.2]METACYCLOPHANES[1]

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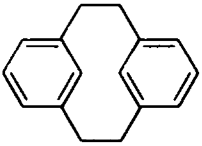
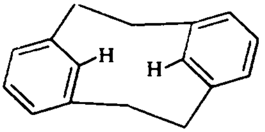
Abstract—The syntheses of di-, tetra- and hexamethyl[2.2]metacyclophanes are described. Their anomalous NMR and UV spectra are discussed in relation to the inherent steric strain in the molecule. The behaviour of the compounds toward homolytic and electrophilic reactions has been examined.

MANY of the unusual properties of [2.2]metacyclophane (I), as revealed by UV and NMR spectra, and by site and course of reactions, are attributable to the highly-strained nature of the molecule.[2,3] The compound has been shown, by the X-ray measurements,[4] to exist in a step-like conformation with two slightly distorted benzene rings, due to steric overcrowding, arranged on parallel planes. The 10-membered ring system forms a rigid chair conformation into which two intraannular hydrogens are extended (I′).



I



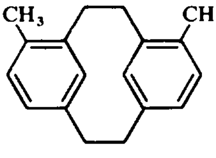
I′

In previous papers,[1,5] we extended the chemistry of I to include several derivatives, and described the synthetic and NMR spectral studies of 4,14-disubstituted derivatives. This paper deals with additional derivatives of I, in which an increasing number of Me groups, up to six, are introduced.

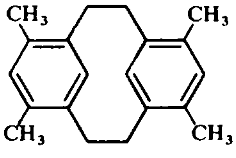
Syntheses and NMR spectra

The Wurtz dimerization of 1,3-bis(bromomethyl)benzene, carried out first by Pellegrin[6] with sodium giving only poor results, furnished[7,8] a 45% yield of I when sodium-tetraphenylethylene adduct was used following the method of Müller and Röscheisen.[9] It was necessary to use high-dilution conditions, which were attained by the combination of low reaction temperature and extended reaction time, in order to eliminate the competing polymerization reaction. This method proved[1,5,10] to be equally suitable for the preparation of derivatives of I. 4,14-Dimethyl[2.2]metacyclophane (II), for example, was prepared[1,5] in a 21% yield.

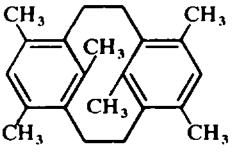
Thus bimolecular condensation (70 hr at −50°) of 4,6-bis(chloromethyl)-*m*-xylene, which was prepared by the bis-chloromethylation[11] of *m*-xylene, afforded, after chromatographical separation, a compound m.p. 204–205°. Elemental analyses and NMR spectra of the compound were in good accord with 4,6,12,14-tetramethyl[2.2]-metacyclophane (III; Tables 1 and 2). The 8,16-proton exhibited an unusual high field shift and adsorbed at δ 4·20 (singlet) due to the ring current effect of the opposite benzene ring extended over it. Further, the bridging methylene signal appeared as an A_2B_2-pattern (δ_A = 1·76, δ_B = 3·22). These spectral features are indicative of a [2.2]metacyclophane structure. The yield of III was 18%. Similarly, 2,6-bis(chloromethyl)mesitylene, obtained by the chloromethylation[11] of mesitylene under forced conditions, afforded a product, m.p. 244°. This compound was assigned the structure



II



III



IV

4,6,8,12,14,16-hexamethyl[2.2]metacyclophane (IV) from analytical data and the NMR spectrum (Tables 1 and 2), which shows a 6-proton singlet at δ 0·48 and a 8-proton A_2B_2-pattern centered at δ 2·78 (δ_A = 2·48, δ_B = 3·10). The unusual shielding shown by the 8,16-Me groups is again attributed to the ring current effect of the opposite benzene ring. An upfield shift of the 8,16-Me signal was also noticed by Boekelheide *et al.*; 8,16-dimethyl- and 8,16-dimethyl-5,13-dimethoxy[2.2]metacyclophanes were reported[12] to show 6-proton Me signals at δ 0·56 and 0·75 respectively.

Since the 10-membered ring system of I exists in a chair form, the bridging methylene signal appears as an A_2B_2-pattern arising from axial and equatorial protons, δ_A (axial) = 2·04, δ_B (equatorial) = 3·05. Consequently, in a compound such as II, in which two ethylene bridges are situated in different environments, there should be

TABLE 1. PHYSICAL PROPERTIES OF [2.2]METACYCLOPHANE DERIVATIVES

Compound	M.p., °C	Formula	Carbon, %		Hydrogen, %	
			Calcd	Found	Calcd	Found
III	204–205	$C_{20}H_{24}$	90·91	90·98	9·09	9·14
IV	244	$C_{22}H_{28}$	90·35	90·00	9·65	9·62
V	148–149[a]	$C_{18}H_{20}$	91·53	91·75	8·47	8·51
VII	218–220	$C_{18}H_{18}Br_2$	54·61	54·48	4·33	4·60
VIII	234–236[b]	$C_{18}H_{16}O_2$				
IX	300	$C_{18}H_{14}N_2$	83·69	83·52	5·46	5·78
X	147	$C_{18}H_{18}$	92·26	92·50	7·74	7·96
XI	165·5–166	$C_{18}H_{17}NO_2$[c]	77·36	77·00	6·13	6·28
XII	292–293	$C_{22}H_{27}NO_2$[d]	78·30	78·24	8·01	7·84

[a] Reported m.p. 147–149°.[14]
[b] Crude material.
[c] Calc: N, 6·13; Found: 5·09.
[d] Calc: N, 4·15; Found: 4·40.

TABLE 2. NMR DATA FOR [2.2]METACYCLOPHANE AND DERIVATIVES[a]

Compound	Solvent	Aryl protons			Methyl protons		Methylene protons			
		5,13-H	6,12,(4,14)-H	8,16-H	8,16-Me	Others	A_2B_2[e]		$A'_2B'_2$[f]	
							eq-H	ax-H	eq-H	ax-H
I[b]	CCl_4	430·8	418·2	254·8 t			182·9	122·7		
II[c]	CCl_4	424·5	411·3	252·9 d			179·5	119·5	197·0	105·6
III	$CDCl_3$	418·8 s		252·0 s		138·0 s			193·2	105·6
IV	$CDCl_3$	397·0 s			28·8 s	141·0 s			189·0	148·2
V	$CDCl_3$		412·0 d	249·0 t		141·0 s	180·9	124·7		
VI[d]	CCl_4		393·0	240·6		225·0 s	177·0	123·6		
VII	$CDCl_3$		432·0 d	257·1 t			188·8	129·2		
IX	DMSO-d_6		456·0 d	268·0 t			196·0	120·0		

[a] The spectra were recorded with a Varian A-60 spectrometer and chemical shifts are expressed in c/s unit relative to internal TMS as 0. Multiplicity is shown as follows: s, singlet, d, doublet, t, triplet.

[b] See Ref. 5.

[c] See Ref. 1.

[d] See Ref. 13.

[e] One of the ethylene bridges without *o*-substituents.

[f] One of the ethylene bridges with *o*-substituents.

two sets of absorption, one corresponding to the substituted side ($A'_2B'_2$), which shows the ethylene bridge with *o*-substituent, and the other the unsubstituted side (A_2B_2). In fact the methylene region of II was observed as an overlap of these two patterns and analyzed as $\delta_A = 1{\cdot}99$, $\delta_B = 2{\cdot}99$ and $\delta_{A'} = 1{\cdot}76$, $\delta_{B'} = 3{\cdot}28$, assuming that the absorption pattern of the unsubstituted side is similar to that of I itself.[1] The spectrum of III shows that this assumption is valid, since this compound possesses only the $A'_2B'_2$-type bridge, which shows an absorption similar to the $A'_2B'_2$-part of II (Fig. 1). Replacement of the 8,16-hydrogens by Me groups as in IV, resulted in further deviation of the spectrum in the methylene region, in spite of the fact that it should be of the $A'_2B'_2$ type. While equatorial protons ($\delta_{B'} = 3{\cdot}10$) absorbed in the expected region, the signal due to axial protons ($\delta_{A'} = 2{\cdot}48$) showed a marked downfield shift presumably due to anisotropy of the 8,16-Me groups, which owing to the steric overcrowding, existed in the proximity of the conformationally locked axial hydrogens.

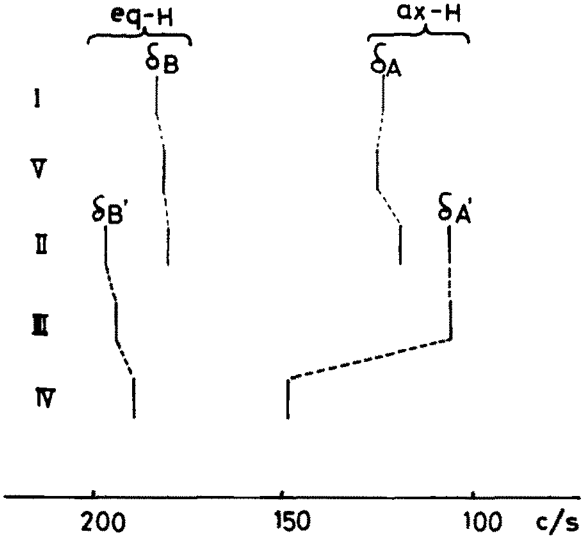
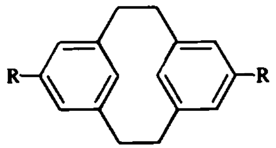


FIG. 1 The chemical shift of axial (δ_A and $\delta_{A'}$) and equatorial (δ_B and $\delta_{B'}$) bridging methylene protons. Unsubstituted and substituted sides are shown by δ_A and δ_B, and $\delta_{A'}$ and $\delta_{B'}$ respectively.

For comparison, 5,13-dimethyl[2.2]metacyclophane (V), m.p. 148–149° was prepared in a 12% yield by a similar method starting from 3,5-bis (bromomethyl)anisole. Earlier preparation of this compound was cited in the review article by Griffin[2] and the NMR spectrum was mentioned in the paper by Boekelheide.[13] More recently, Allinger *et al.*[14] achieved the preparation of V using phenyllithium as a condensing agent. The compound we obtained had physical properties entirely consistent with these authors. NMR spectral measurements showed that the intraannular 8,16-proton absorbed at δ 4·15 and bridging methylene group appeared as an A_2B_2-pattern ($\delta_A = 2{\cdot}08$, $\delta_B = 3{\cdot}02$) similar to the A_2B_2-pattern of I and II (Fig. 1).

By means of 4,14-disubstituted derivatives, we have examined the dependence of aryl and methylene proton signals on the nature of the substituents. In order to find a similar correlation, several 5,13-disubstituted derivatives were prepared. Except for compound V, 5,13-dimethoxy derivative (VI)[2, 13] is the only compound hitherto known. The treatment of V with 2 moles of NBS in carbon tetrachloride afforded 5,13-bis(bromomethyl)[2.2]metacyclophane (VII), m.p. 218–220°, in a 68% yield. No bromination occurred at the bridging methylene group. Treatment of VII with 2-nitropropane and sodium ethoxide in DMSO afforded [2.2]metacyclophane-5,13-dicarbaldehyde (VIII), m.p. 234–236°, in a 59% crude yield. Without further purification, VIII was treated with hydroxylamine hydrochloride in pyridine to obtain the dioxime, which, on heating with acetic anhydride, was converted to 5,13-dicyano-[2.2]metacyclophane (IX). The overall yield from dialdehyde VIII was 27%. The structural proof for these compounds was obtained by elemental analyses, IR and NMR spectra (Tables 1 and 2). The appearance of an NMR signal, assignable to the 8,16-proton, at δ 4·15–4·35 as a triplet (J = 1·8 c/s) indicated that during these transformations the [2.2]metacyclophane structure was not affected.



V : R = Me
VI : R = OMe
VII : R = CH_2Br
VIII : R = CHO
IX : R = CN

The 8,16-proton signals experienced a small yet definite downfield shift on going from the dimethoxy derivative VI to the dinitrile IX. This may be explained by the combination of mesomeric effect exerted by substituent as well as the change in the ring current of the opposite benzene ring also affected by the introduction of a substituent. The linear correlation between the chemical shift and Hammett σ constant obtained for the axial and equatorial methylene protons was not good, in contrast to the 4,14-disubstituted derivatives where strong dependence of chemical shift on the nature of substituent was demonstrated.[1]

UV absorption spectra

The anomalous UV spectra of short-bridged paracyclophanes have been interpreted[15, 16] in terms of transannular interaction between the two aromatic rings and deformation in the molecular structure due to steric compression. Comparison of the spectra of [2.2]metacyclophane (I) with those of the open-chain compound, 3,3′-dimethyl-bibenzyl, revealed[17] that the benzenoid band of I appeared as a broad peak without fine structure shifted to longer wavelength with intensity decrease, characteristic to bent benzene, and that there was a hidden band ascribable to transannular electronic interaction for which absorptivity in the 225–250 mμ region was unusually high.

TABLE 3. COMPARISON OF THE BENZENOID BAND BETWEEN [2.2]METACYCLOPHANES AND CORRESPONDING ALKYLBENZENES

Compound	λ_{max}, mμ	ε	$\varepsilon/2$	Solvent	Compound	λ_{max}, mμ	ε	Solvent
I	270	570	285	hexane	*m*-xylene[a]	266	400	hexane
II	276	673	337	hexane	1,2,4-trimethylbenzene[a]	275	835	hexane
V	277	552	276	ethanol	mesitylene	266	243	ethanol
III	281	656	328	hexane	1,2,4,5-tetramethylbenzene[a]	279	820	hexane
IV	290	504	252	hexane	pentamethylbenzene[a]	270	365	hexane

[a] Taken from A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry* (2nd Edition) p. 134. Edward Arnold, London (1958).

In this section, UV spectra of [2.2]metacyclophanes substituted with an increasing number of Me groups are compared with those of simple benzene derivatives representing the half metacyclophane structure, the bridging methylene group of which is replaced by Me groups. Although they are not ideal model compounds for rigorous intensity comparison, by using one half of molar absorptivity for metacyclophane series, any serious deviation from the spectra of the corresponding benzene compounds might become a good measure for detecting deformations in the molecule or electronic anomality. Data for the benzenoid band are tabulated in Table 3. A significant difference between these two series is the absence of fine structure in the metacyclophanes in contrast to the benzene derivatives, band maximum of which is determined as an approximate center of the fine structure.

In the Me substituted benzene derivatives, the absorption maximum and band intensity are correlated with the number and position of the Me groups. Namely, whereas an introduction of an Me group in the *meta* position of *m*-xylene does not alter the spectrum (see mesitylene), substitution of one or two Me groups in the *ortho/para* positions results in a bathochromic shift accompanied by more than a twofold increase in the intensity (compare 1,2,4-trimethylbenzene or 1,2,4,5-tetramethylbenzene with *m*-xylene). Further introduction of Me groups, however, results in the hypsochromic shift with intensity decrease (compare pentamethylbenzene with 1,2,4,5-tetramethylbenzene), since three or more vicinal Me groups in the benzene nucleus may push a sandwiched Me group out of the benzene plane thus eliminating its contribution to the electronic excitation.

While the absorption maxima deviated markedly in Me substituted benzene derivatives, it is significant that those of metacyclophanes display a steady bathochromic shift with increase of Me groups. Molar absorptivities, however, are found to remain in a narrow range of 250–340 ($\varepsilon/2$).

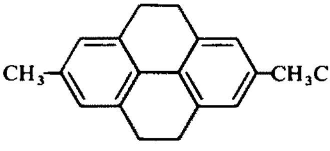
The comparison of the spectra between each of the corresponding pairs revealed that metacyclophanes always exhibit absorption maximum at longer wavelength than the benzene derivatives. The bathochromic shift is especially prominent with IV and V, amounting to 10 mμ and 11 mμ respectively. The intensity of the band maximum is much smaller in II and III, than 1,2,4-trimethylbenzene.

These deviations, bathochromic shift accompanied by intensity decrease, found for the metacyclophane series are best interpreted as being due to inherent non-planality of the benzene rings and deformation of bridging methylene groups out of the benzene plane. Especially noteworthy is the large bathochromic shift displayed by going from III to IV, in spite of the fact that in the corresponding benzene derivatives an hypsochromic shift of 9 mμ is observed. This result suggests the presence of an even larger molecular deformation in IV due to steric overcrowding at the 8,16-positions by the replacement of the bulky Me groups by hydrogen.

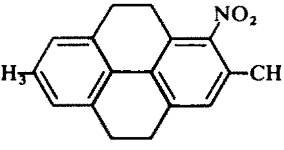
The photochemical and electrophilic substitution reactions

Besides the electronic interaction between the two benzene rings, which is common for lower members of cyclophanes, [2.2]metacyclophane (I) is unique in radical and electrophilic reactions. We have already reported the facile photochemical transannular reaction of I, induced by iodine,[7] to give 4,5,9,10-tetrahydropyrene and further dehydrogenation products. In spite of the formal resemblance, the reaction is assumed to proceed by a mechanism different from the well established *cis*-stilbene-phenanthrene reaction[19] since two benzene rings in I are not in conjugation. The reaction with nitrosyl chloride under irradiation also produced the transannular reaction product. While attempted iodination with iodine-silver perchlorate[7,18] afforded 4,5,9,10-tetrahydropyrene, bromination,[14] iodination (iodine-nitric acid)[18] or nitration[8,17] produced 2-substituted 4,5,9,10-tetrahydropyrene derivatives.

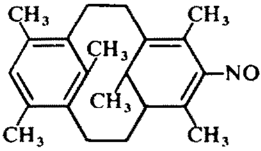
Since the mechanistic details and also the scope of these transannular reactions are not clear, we submitted dimethyl and hexamethyl derivatives of I to similar reactions. The UV irradiation of the dimethyl derivative V, in the presence of iodine, was carried out in a quartz vessel using a 1-kW high-pressure mercury arc lamp for 48 hr. In addition to the starting material (74% recovery), a compound, m.p. 147° was obtained. The NMR spectrum of this compound shows three singlets at δ 2·36 (methyl), 2·87 (methylene) and 6·96 (aryl) in a ratio of 3:4:2. The disappearance of a characteristic peak of V at δ 4·06 (8,16-H) indicates the occurrence of the transannular reaction. These data coupled with analytical figures suggested that the compound is 2,7-dimethyl-4,5,9,10-tetrahydropyrene (X), which was formed in a 26% yield.



X



XI



XII

On the other hand, no reaction occurred when IV was irradiated under similar conditions, the starting material being largely recovered.

The attempted iodination of V with iodine and silver perchlorate furnished a 26% yield of X. While the treatment of V with 9N HNO_3 for 3 min resulted in complete recovery of the starting material, more concentrated HNO_3 (12N) afforded a small amount of X and a nitro-compound, m.p. 165·5–166°. From the NMR spectrum, which displayed absorptions at δ 7·02 (3-aryl), 6·97 (6,8-aryl), 2·86 (two peaks, 9,10-methylene) and 2·33 (singlet, methyl) the compound was assumed to be 1-nitro-2,7-dimethyl-4,5,9,10-tetrahydropyrene (XI). After completion of this work, Allinger *et al.*[14] disclosed similar studies. The physical properties of X and XI are in good agreement with those reported. The treatment of V with concentrated nitric acid, which had been reported[14] to produce a 20% yield of X, furnished a 74% yield of X. We also confirmed the smooth conversion of X to XI on nitration with 12N HNO_3 (62% yield). Development of an intense violet color during nitration of V may indicate that nitration proceeds through formation of a charge-transfer complex. No such coloration occurred in the nitration of I and IV (below). Further refinement of the nitration reaction mechanism[8] is under consideration.

From these results it was concluded that iodination or nitration of V produced 2,7-dimethyl-4,5,9,10-tetrahydropyrene X as an initial reaction product. The formation of 2-substituted derivative (such as XI) is then assumed to be due to further substitution of X. The presence of Me groups at the 8,16-position may hinder the transannular reaction as was observed in the photolytic studies. The treatment of IV with 12N HNO_3 afforded a mononitro compound, m.p. 292–293°. The fact that the product, 5-nitro-4,6,8,12,14,16-hexamethyl[2.2]metacyclophane (XII), preserved the metacyclophane structure was shown by the NMR spectrum, which consists of signals at δ 0·51 and 0·56 (both singlet, 8,16-Me) 2·26 (singlet, 12,14-Me), 2·31 (singlet, 4,6-Me), ca 2·23 (center of methylene) and 6·61 (singlet, aryl).

EXPERIMENTAL*

4,6,12,14-*Tetramethyl*[2.2]*metacyclophane* (III)

A soln of 14 g (0·069 mol) of 2,4-bis(chloromethyl)-*m*-xylene, m.p. 99° (lit.[20] 99°), obtained[20] by bis-chloromethylation of *m*-xylene, in 750 ml THF was added dropwise through a specially designed precision dropping funnel to a soln of sodium-tetraphenylethylene adduct, which was prepared from 8·0 g Na (excess) and 3·5 g (0·011 mol) tetraphenylethylene in 200 ml of abs THF, in the course of 70 hr at −50° under a current of N_2. When the addition was complete, a small amount of MeOH was added and the resulting mixture was filtered to remove excess Na and NaCl. The residue was washed with ether and combined with a concentrate of the filtrate. After washing with water, the ethereal soln was dried, and concentrated to give yellow solid, which was dissolved in $CHCl_3$ and subjected to column chromatography on alumina using $CHCl_3$ as an eluent. From the first elute a colorless solid was isolated and dissolved in ligroin and rechromatographed with n-hexane. The resulting colorless plates were recrystallized from EtOH to give 1·17 g (18%) of the product, m.p. 205–206°.

4,6,8,12,14,16-*Hexamethyl*[2.2]*metacyclophane* (IV)

Following a similar procedure, a soln of 28 g (0·13 mol) of 2,4-bis(chloromethyl)mesitylene, m.p. 102–103° (lit.[21] 102–103°), which was prepared[21] from mesitylene by bis-chromethylation, in 300 ml abs THF, was added in the course of 70 hr to the condensing reagent, made from 8·0 g (excess) Na and 5·0 g (0·015 mol) tetraphenylethylene in 300 ml THF. The reaction was carried out at −40° under a current of N_2. After working up as above, the product was taken up in ligroin and chromatographed on alumina using n-hexane as an eluent. Compound IV was obtained as colorless plates, m.p. 244° and recrystallized from EtOH, in a yield of 5% (950 mg).

5,13-*Dimethyl*[2.2]*metacyclophane* (V)

A soln of 30 g (0·11 mol) 3,5-bis(bromomethyl)toluene, m.p. 58–60° (lit.[22] 60–61°), dissolved in 700 ml THF was added to sodium-tetraphenylethylene adduct, prepared from 10 g (excess) Na and 3·5 g (0·011 mol) tetraphenylethylene at −40 to −70°, in the course of 70 hr yielding 153 mg (12% yield) of V as colorless needles, m.p. 148–149° (lit.[14] 147–149°).

5,13-*Bis*(*bromomethyl*)[2.2]*metacyclophane* (VII)

To a soln of 230 mg (0·98 mmol) V in 20 ml CCl_4, 0·41 g (2·3 mmol) NBS and a few mg of benzoyl peroxide were added. After being heated under reflux for 2·5 hr, the mixture was filtered and the filtrate concentrated to about 7 ml. The crude material, obtained as colorless needles, after repeated recrystallizations from CCl_4 melted at 218–220°, the yield 68%.

[2.2]*Metacyclophane*-5,13,*dicarbaldehyde* (VIII)

A NaOEt soln, made from 0·24 g (9·6 mg atom) Na and 8·2 ml EtOH, containing 0·87 g (8·8 mmol) 2-nitropropane was added to a soln of 1·03 g (2·6 mmol) of VII dissolved in 60 ml DMSO in the course of 30 min. The reaction mixture was kept at room temp for 2·5 hr under stirring, then diluted with 500 ml water and allowed to stand overnight in a refrigerator. The crude material, m.p. 234–236°, 393 mg (58% yield), was collected as yellow powder; ν_{max}^{CO} 1688 cm^{-1}.

5,13-*Dicyano*[2.2]*metacyclophane* (IX)

A mixture of 170 mg (0·65 mmol) of VIII, 180 mg (3·8 mmol) hydroxylamine hydrochloride in 10 ml pyridine–ethanol (1:1) was warmed at 40° for 24 hr. After concentration, the dioxime was obtained as a colorless solid, which contained a small amount of nitrile as evidenced by the additional absorption occurring at 2200 cm^{-1}. Without further purification, the material was refluxed with 15 ml Ac_2O for

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[*] All m.ps are uncorrected. Analytical, NMR and UV data are compiled in Tables 1, 2 and 3 respectively. Gas chromatography was carried out by using Hitachi K-53 equipped with 3·3 ft 5% XE-60 silicon gum rubber on Chromosorb W column.

3 hr. After cooling, dinitrile IX (45 mg; 27% yield) was obtained as colorless needles, m.p. >300°, recrystallized from EtOH; ν_{max}^{CN} 2200 cm^{-1}.

Irradiation reaction of V

A mixture of 62 mg (0·26 mmol) of V, 41 mg (0·16 mmol) I_2 and 72 mg (excess) $NaHCO_3$ and 30 ml cyclohexane in a quartz vessel was irradiated with a 1 kW high-pressure mercury arc lamp immersed in a circulating water jacket. After 48 hr irradiation, the mixture was analyzed by gas chromatography using 3·3 ft 5% XE-60 silicon gum rubber on Chromosorb W column at 150°. In addition to a peak with retention time of 10 min which correspond to that of V, a small peak appeared with retention time of 30 min. By using authentic material the latter peak was found to be due to X, which was formed in a 26% yield.

Irradiation reaction of IV

A soln of 120 mg (0·41 mmol) of IV, 78 mg (0·31 mmol) I_2 and 140 mg (excess) $NaHCO_3$ in 60 ml cyclohexane was irradiated for 48 hr using the same apparatus as above. The reaction mixture was analysed by gas chromatography using the above conditions. The only peak detected was due to the starting material, retention time of which was 11 min. Chromatography on alumina and elution with n-hexane gave 104 mg of starting material, m.p. 244°.

Attempted iodination of V

I_2 (60 mg, 0·24 mmol) was added to a stirred suspension of 62 mg (0·26 mmol) of V and 60 mg (0·30 mmol) silver perchlorate in 8 ml ether. The stirring was continued for 2 hr and the mixture then heated under reflux for 2 hr. The ppt was washed with ether and the ethereal soln combined with the filtrate. Chromatography on alumina of the concentrate using n-hexane as eluent, yielded 35 mg of starting material, m.p. 146°, and 8 mg of X. Since intermediate fractions contained mixtures of V and X and the complete separation of these was difficult, therefore the product was examined by gas chromatography using the same column as above operated at 150°. Two peaks having retention times of 11 and 33 min appeared and were assigned V (74%) and X (26%) by comparison with authentic materials.

Reaction of V *with nitric acid*

(a) To a soln of 186 mg (0·86 mmol) of V in 18 ml glacial AcOH, 6 ml 12N HNO_3 was added at room temp and the soln was kept stirred for 3 min. The soln was then poured onto ice cubes. The ppt was collected, washed with water and dried. The product was taken up in ligroin and submitted to column chromatography on alumina using n-hexane with increasing amounts of benzene as eluent, yielding 108 mg (48% yield) of XI, m.p. 165·5–166° (lit.[14] 167–169°) as yellow needles; $\nu_{max}^{NO_2}$ 1520 and 1372 cm^{-1}.

(b) To a stirred soln of 450 mg (1·9 mmol) V in 96 ml glacial AcOH, was added a solution of 3·3 ml conc HNO_3 in 2·1 ml glacial AcOH during 3 min. After stirring for 2 min, it was poured into ice water. The collected material was dissolved in ligroin and subjected to alumina column chromatography and eluted successively with n-hexane, 1:1 n-hexane–benzene and benzene. Elution with n-hexane afforded 392 mg (74% yield) of X, m.p. 145–147°, recrystallized from EtOH. When the eluate was changed to n-hexane–benzene, 13 mg (2·5% yield) of light yellow needles, m.p. 165–166° (recrystallized from EtOH), identical with authentic XI, were obtained.

Nitration of X

Nitric acid (12N; 3·5 ml) was added to a stirred soln of 111 mg (0·55 mmol) of X dissolved in 11 ml glacial AcOH and kept for 3 min.

Column chromatography yielded a yellow solid which was recrystallized from EtOH to give 91 mg (62% yield) of XI, m.p. 165°, identical with an authentic specimen.

Reaction of IV *with nitric acid*

Nitric acid (12N; 6 ml) was added to a stirred soln of 198 mg (0·68 mmol) of IV in 40 ml glacial AcOH and kept for 3 min as above. Chromatography on alumina carried out as above furnished a yellow solid, which was recrystallized from benzene to give 74 mg (30% yield) of XII, m.p. 292–293° as pale yellow needles; $\nu_{max}^{NO_2}$ 1524 and 1378 cm^{-1}.

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