

Thermal Decomposition of 9-(Substituted phenylimino)-1,4-dihydro-1,2,3,4-tetraphenyl-1,4-methanonaphthalenes

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Addition of benzyne to the tetraphenylcyclopentadienone anils (4a—f) gives the 9-(substituted phenylimino)-1,4-dihydro-1,2,3,4-tetraphenyl-1,4-methanonaphthalenes (5a—f) which on thermolysis eliminate the phenyl isocyanides (6a—f). By following the appearance of isocyanide the relative rates of decomposition in toluene at 120.0° are (5a) : (5b) : (5c) : (5d) : (5e) : (5f) = 2.20 : 1.69 : 1.00 : 0.26 : 0.18 : 1.19 and lead to the conclusion that elimination is slow by comparison with the rate of inversion at nitrogen.

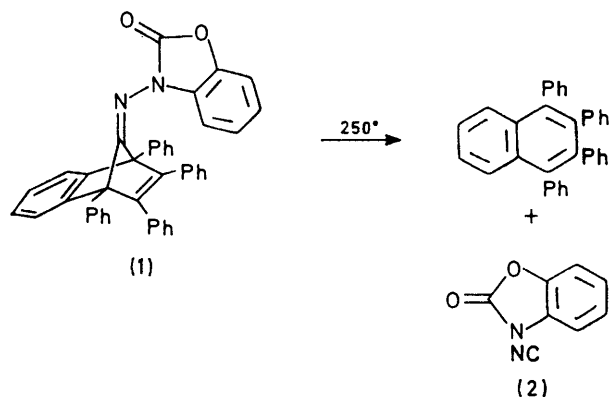
THE 1,4-dihydro-1,4-methanonaphthalen-9-one hydrazone (1) is surprisingly stable to heat.¹ Whereas decarbonylation of 1,4-dihydro-1,4-methanonaphthalen-9-one precludes its isolation,² the hydrazone (1) was re-

¹ R. S. Atkinson, A. J. Clark, and R. E. Overill, *Chem. Comm.*, 1971, 535.

covered in 46% yield after heating for 4 h in boiling decalin (192°). The anticipated decomposition of (1)

² G. Wittig and E. Knauss, *Chem. Ber.*, 1958, **91**, 895. A stable manganese carbonyl complex of 1,4-dihydro-1,4-methanonaphthalen-9-one has recently been prepared: D. Wege and S. P. Wilkinson, *J.C.S. Chem. Comm.*, 1973, 795.

does occur readily at 250°, although the *N*-isocyanide (2) was not isolated since it apparently undergoes further



reaction with the other fragmentation product, 1,2,3,4-tetraphenylnaphthalene.

To explain the thermal stability of (1), it was suggested that ejection of the *N*-isocyanide (2) was a cheletropic elimination³ in which a linear geometry of (bridge C)=N-N was required to permit stabilisation of the incipient carbene as an isocyanide. This particular geometry is itself the transition state for lateral inversion at the imino-nitrogen and the thermal stability of (1) may therefore be correlated with its expected slow inversion rate.

If this suggestion is correct then replacement of the benzoxazolone substituent in (1) by a group which accelerates the inversion at the trigonal (sp^2) nitrogen should reduce the thermal stability of the compound. This paper reports the synthesis of the substituted 1,4-dihydro-1,4-methanonaphthalen-9-one anils (5a-f) and a study of their thermal decomposition.

RESULTS AND DISCUSSION

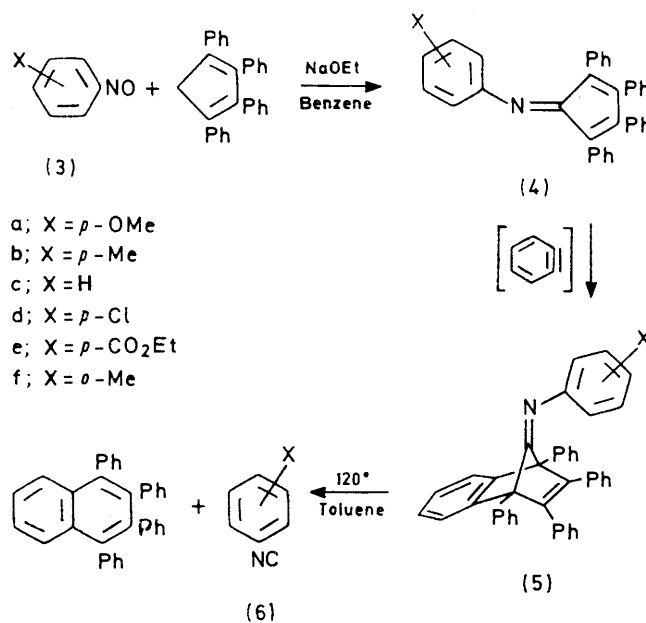
The anils (5a-f) were obtained by the route outlined in the Scheme. The appropriate substituted nitrosobenzenes (3a-f) were prepared by published methods, and were condensed with tetraphenylcyclopentadiene in the presence of sodium ethoxide to yield the characteristically red-brown crystalline tetraphenylcyclopentadienone anils (4a-f).⁴ Compound (4c) has previously been prepared by a different route.⁵ Reaction of compounds (4a-f) with benzyne, generated by lead tetra-acetate oxidation of 1-aminobenzotriazole,⁶ gave the crystalline adducts (5a-f) in good yields. The mass spectra of all these compounds contain an intense ion at m/e 432, corresponding to loss of the bridging group XC_6H_4NC .

In contrast to the thermal decomposition of (1), the aromatic isocyanides (6a-f) formed on heating (5a-f) react slowly, if at all, with tetraphenylnaphthalene at the decomposition temperature and can be detected by their repulsive odours. The identity of the isocyanide from each of the anils (5a-f) was confirmed by comparison of its g.l.c. retention time with that of an authentic specimen.

* Although this further reaction may possibly involve tetraphenylnaphthalene, we consider that the isocyanides (6) are unstable even in the absence of tetraphenylnaphthalene.

The rates of the thermal decomposition of the anils (5a-f) were examined in solution in toluene. Portions (3 μ l) of a solution of the anil (5 μ mol) and a suitable g.l.c. internal standard (1.3-3.9 μ mol) in toluene (50 μ l) were sealed in melting-point tubes and totally immersed in a thermostatted oil-bath at 120.0°. Tubes were removed at intervals and cooled rapidly to halt decomposition. The contents of each tube were analysed by g.l.c., the area of the isocyanide product peak being measured relative to the area of the internal standard peak.

Attempts to obtain infinity values for the areas of the isocyanide peaks, by allowing decomposition of the anils to proceed for 45 min at 170°, were frustrated by further reaction of the isocyanides: * thus in every case except (5d) the resulting isocyanide peak was *smaller* than the isocyanide peaks observed after long reaction times at 120°. However, satisfactory linear first-order plots



SCHEME

(Figure) for the appearance of isocyanide were obtained by taking as infinity values the maximum values observed at 120°: the time at which the maximum isocyanide peak was observed was in no case less than 4.4 times the (subsequently-determined) half-life of the anil. Moreover, having prepared authentic specimens of the aromatic isocyanides (6a-f), the g.l.c. detector response for each isocyanide could be determined relative to the response for the appropriate internal standard, and thus it was possible to confirm that in each case the infinity value used represented at least 90% of the infinity value calculated on the assumption that 1 mol of anil decomposes to 1 mol of isocyanide. The first-order rate constants (k) for decomposition of the anils (Table 1) were

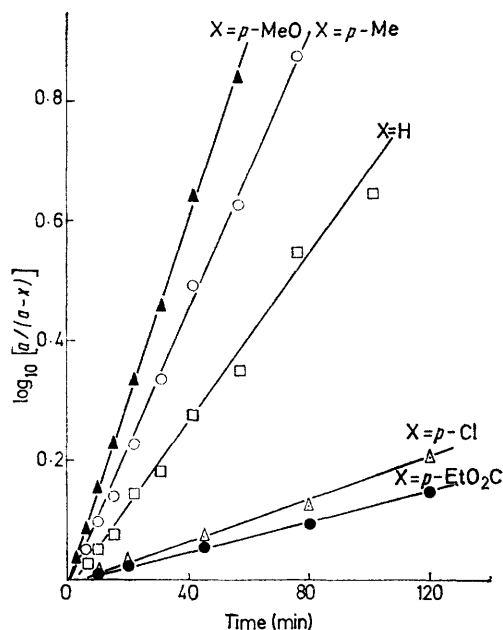
³ R. W. Hoffmann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 529.

⁴ K. Ziegler and B. Schnell, *Annalen*, 1925, **445**, 266.

⁵ B. H. Freeman, D. Lloyd, and M. I. C. Singer, *Tetrahedron*, 1972, **28**, 343.

⁶ C. D. Campbell and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 742.

deduced from 7 to 9 determinations of isocyanide at intervals extending over 1–3 half-lives. The results for (5a–e) are presented graphically in the Figure; for

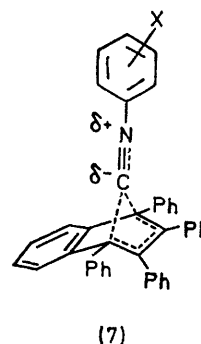


Plots of $\log_{10}[a/(a-x)]$ vs. time for the decomposition of the anils (5a–e) in toluene at 120.0° (x = g.l.c. peak area of isocyanide product relative to peak area of internal standard; $a = x$ at infinite time)

convenience of scale, the following points, which lie on their respective lines, have been omitted:

Anil	(5d)	(5d)	(5d)	(5e)	(5e)
Time (min)	168	225	300	168	225
$\log_{10}[a/(a-x)]$	0.280	0.366	0.533	0.201	0.284

Replacement of the benzoxazolone substituent in (1) by a phenyl group would be expected to increase the rate of inversion at the trigonal (sp^2) nitrogen.⁷ Relative to an alkyl group, the benzoxazolone substituent is known



prediction made earlier. Closer inspection of the first-order rate constants (Table 1), however, reveals that electron-donating substituents in the phenyl group cause a small increase in the rate of decomposition whereas electron-withdrawing substituents have the opposite effect. Rates of inversion in various *p*-substituted anils ($p\text{-XC}_6\text{H}_4\text{-N=C}$) have been studied¹⁰ and electron-donating substituents found to reduce the rate of inversion whereas electron withdrawing substituents increase it. Evidently there is a contradiction here between the observed relative rates of decomposition of the anils (5a–f) and the predicted relative rates based on consideration of ease of inversion at the sp^2 nitrogen alone. Furthermore, the effect of *ortho*-substitution is normally to lower the inversion barrier,⁷ whereas the *o*-methyl-substituted anil (5f) decomposes less quickly than does its *p*-substituted isomer (5b). This again suggests that the ease of attainment of collinearity at the imino-nitrogen is not the dominant factor in determining the rate of elimination from (5a–f).

To accommodate these results we suggest that for the anils (5a–f), elimination is slow by comparison with the rate of inversion at nitrogen. The substituent effect may

then be correlated with an increase in positive charge at the imino-nitrogen as the isocyanide develops (7).

TABLE 1

Decomposition of 1,4-dihydro-1,2,3,4-tetraphenyl-1,4-methanonaphthalen-9-one anils in toluene at 120.0°

Anil	$10^3k/\text{min}^{-1}$	Internal standard	Molar ratio standard : anil	G.l.c. column temperature ^a (deg)	G.l.c. retention time (min) ^a	Standard	Isocyanide
(5a)	34.5	Tetralin	0.52	136	2.8	4.3	4.3
(5b)	26.6	n-Butylbenzene	0.42	105	2.9	4.1	4.1
(5c)	15.7	n-Butylbenzene	0.79	87	6.0	4.2	4.2
(5d)	4.01	n-Butylbenzene	0.31	117	1.9	3.6	3.6
(5e)	2.88	2-Methylnaphthalene	0.26	140	3.5	6.0	6.0
(5f)	18.7	<i>p</i> -Cymene	0.38	96	3.2	4.5	4.5

^a G.l.c. analyses were performed using a Pye 104 flame ionisation chromatograph with a 1.5 m \times 4 mm i.d. glass column containing 3% Silicone OV17 on silanised 100–120 mesh Diatomite C. The nitrogen carrier flow rate was 50–55 ml min^{-1} . Samples were introduced by on-column injection.

to retard inversion in aziridines whereas a phenyl group accelerates it.⁸ This effect is likely to be reproduced in inversion at sp^2 hybridised nitrogen, where a reduced rate has been observed with other electron-withdrawing non-conjugating groups.⁹ The lower thermal stability of the anils (5a–f) relative to (1) is thus in agreement with the

⁷ H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.

⁸ R. S. Atkinson, *Chem. Comm.*, 1968, 676; G. Szeimies and R. Huisgen, *Chem. Ber.*, 1966, **99**, 491; A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5203.

A similar explanation for the stability of (1) may be inadequate and the lower rate of inversion could be the factor responsible for its thermal stability.

⁹ H. Kessler and D. Leibfritz, *Tetrahedron*, 1970, **26**, 1805; C. I. Stassinopoulou, C. Zioudrou, and G. J. Karabatsos, *Tetrahedron Letters*, 1973, 3671.

¹⁰ H. Kessler, *Tetrahedron Letters*, 1968, 2041; H. Kessler, P. F. Bley, and D. Leibfritz, *Tetrahedron*, 1971, **27**, 1687; G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Phys. Chem.*, 1965, **69**, 1584. See however, G. E. Hall, W. J. Middleton, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 4778.

A less satisfactory alternative explanation of the decomposition of the anils (5a—f) involves rate-determining homolysis of one of the bridge bonds, but it becomes difficult to rationalise the relative rates of decomposition on that basis. We have considered only the lateral shift mechanism for inversion at nitrogen in (5a—f); inversion by the rotational mechanism would never result in $\text{>C=N-C}_6\text{H}_4\text{X}$ attaining collinearity.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded as Nujol mulls. Mass spectra were obtained using an A.E.I. MS9 spectrometer. Alumina was Spence type H. Light petroleum refers to the fraction b.p. 60—80°.

The compounds had the following m.p.s: (4a) 207—208°, (4b) 101—103°, (4c) 235—238° (lit.,⁵ 235°), (4d) 106—109°, (4e) 174—176°, and (4f) 195—198°.

1,4-Dihydro-1,2,3,4-tetraphenyl-1,4-methanonaphthalen-9-one Anils (5a—f).—The general procedure is illustrated for the case of (5f). The tetraphenylcyclopentadienone anil (4f) (0.250 g) and 1-aminobenzotriazole (0.100 g) were dissolved in dichloromethane (2.5 ml) and a solution of lead tetra-acetate (0.365 g) in dichloromethane (2 ml) added dropwise with vigorous stirring. After separation of lead diacetate, the solvent was evaporated off and the residue crystallised from benzene—light petroleum to give the anil (5f) (0.189 g, 65%) as needles. Other anils were prepared similarly and crystallised from benzene—light petroleum or benzene—ethanol. In some cases traces of the coloured

TABLE 2
I.r. and analytical data for anils (5)

Anil	$\nu_{\text{C=N}}/\text{cm}^{-1}$	Found (%)			Formula	Required (%)		
		C	H	N		C	H	N
(5a)	1708	86.7	5.4	2.4	$\text{C}_{42}\text{H}_{31}\text{NO}$	86.7	5.2	2.25
(5b)	1710	91.75	5.7	2.55	$\text{C}_{42}\text{H}_{31}\text{N}$	91.65	5.8	2.55
(5c)	1726, 1710	91.8	5.55	2.65	$\text{C}_{41}\text{H}_{29}\text{N}$	91.95	5.5	2.6
(5d)	1703	86.35	4.95	2.45	$\text{C}_{41}\text{H}_{28}\text{ClN}$	86.95	5.15	2.4
(5e)	1731, 1700	86.95	5.45	2.3	$\text{C}_{44}\text{H}_{33}\text{NO}_2$	87.35	5.65	2.2
(5f)	1717	91.75	5.7	2.55	$\text{C}_{42}\text{H}_{31}\text{N}$	91.85	5.75	2.5

Tetraphenylcyclopentadiene was prepared by the method of Ziegler and Schnell.⁴ Substituted nitrosobenzenes (3a—f) were obtained by published methods.

2,3,4,5-Tetraphenylcyclopentadienone Anils (4a—f).—*General Procedure.* By using a variation of the method given by Ziegler and Schnell,⁴ tetraphenylcyclopentadiene (2 mmol) and the aromatic nitroso-compound (4 mmol) were heated to boiling in benzene (15 ml) and then treated with sodium ethoxide in ethanol (0.030 g sodium in 0.5 ml ethanol). A deep red-brown colouration occurred immediately. The mixture was heated under reflux for 2 min and after cooling, was added to the top of a column of alumina made up in benzene. The anils were eluted as brown bands and, after evaporation of the eluant, were crystallised from benzene—ethanol or benzene—light petroleum giving red-brown solids in 15—25% yield. In the preparation of (4e), methyl *p*-nitrosobenzoate was used as the aromatic nitroso-compound, but the n.m.r. spectrum of the product showed that ester exchange had occurred with the sodium ethoxide—ethanol used in the condensation.

starting anil (4) persisted in the adduct (5) even after crystallisation. These traces were conveniently removed by hydrogenation in the presence of palladium—charcoal (10%) in benzene, a procedure which leaves the adducts (5) unaffected. All the pure anils (5) melted at *ca.* 180° (decomp.), the precise value of the m.p. depending on the rate of heating. The i.r. and analytical data are in Table 2.

Aryl Isocyanides (6a—f).—Authentic samples were prepared from the corresponding aryl formamides by the method of Ugi and Meyr.¹¹ *p*-Ethoxycarbonylphenyl isocyanide was obtained in low yield following the general procedure of Walborsky and Niznik;¹² crystallisation from light petroleum gave needles, m.p. 37—37.5°, ν_{max} 2134s, 2122sh, and 1718s, br cm^{-1} , δ (CCl_4) 1.40 (t, *J* 7 Hz, Me), 4.39 (q, *J* 7 Hz, CH_2), and 7.36, 7.50, 8.02, and 8.16 (aromatic AA'BB', 4 major lines).

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¹¹ I. Ugi and R. Meyr, *Chem. Ber.*, 1960, **93**, 239.

¹² H. M. Walborsky and G. E. Niznik, *J. Org. Chem.*, 1972, **37**, 187.