

# SYNTHESIS OF BRANCHED AZOALKANES AND KINETICS OF THEIR THERMAL DECOMPOSITION\*

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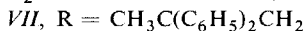
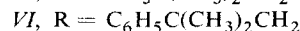
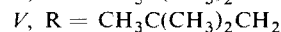
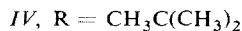
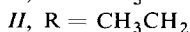
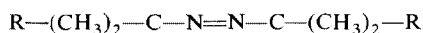
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Symmetrical azo compounds with strongly branched alkyl groups joined through a tertiary carbon atom to the nitrogen atoms of the azo group were synthesized. The kinetics of thermal decomposition of these compounds in solution was measured and the results were used in the evaluation of the effect of the steric order on their stability.

A number of authors have studied the thermal decomposition of azo compounds from the standpoint of its dependence on structure, with a special attention to the inductive, resonance, and steric effects. Because of the easy preparation of tertiary azo compounds, these papers (with the exception of some recent ones<sup>1-5</sup>) were predominantly concentrated on azo compounds having a nitrile group bonded on the  $\alpha$ -carbon atom with respect to the azo group<sup>6-12</sup>. The nitrile group strongly affects the stability of the azo compounds by its inductive and resonance influence, reduces their decomposition temperature and increases the rate of decomposition.

To rule out the above effects as far as possible and to study only the steric effects, we used azo compounds *I-VII*. All the compounds investigated here were prepared by oxidation of the respective amines with iodine pentafluoride. As the yields of *VI* and *VII* were too low (below 10%), they were prepared by methods yielding better



results. *VI* was prepared by oxidizing N,N'-bis(2,4-dimethyl-4-phenyl-2-pentyl)-sulphamide with tert-butyl hypochlorite; *VII* was obtained by substituting chlorine in the respective chloro derivative with the methyl group by means of CH<sub>3</sub>MgBr. The necessary starting amines were obtained by alkylation of urea with tertiary alcohols followed by hydrolysis, or *via* Ritter's reaction from tertiary alcohols

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followed by hydrolysis of the resulting formamides at an elevated pressure. The compounds were identified by elemental analysis, NMR and UV spectroscopy.

To characterize and evaluate steric effects of variously bulky alkyl groups attached to the azo group, the first three compounds of the series under investigation (*I*, *II*, *III*) (ref.<sup>13,14</sup>) were used as standards to which changes in the kinetic parameters of the thermal decomposition of other branched compounds were related. In these three compounds the alkyl groups are attached through the tertiary carbon atom to the azo group similarly to the other compounds, but unlike the latter they are not branched any further. In view of their structure there is no reason for great differences in the influence of the induction effects on their stability. A somewhat higher rate of the decomposition of *III* is due to a moderate interaction of the end methyl groups on both halves of the molecule. In other compounds, which possess branched alkyl groups, the steric effects become operative. These compounds can be derived from the former three basic compounds by substituting hydrogen atoms with alkyl groups; the molecules are bulkier, the methyl groups are closely packed to each other, their rotation is slightly suppressed, a weaker effect of the B-strain is reflected in an accelerated decomposition. The methyl groups in compound *V* are agglomerated in such a way that their rotation is greatly restricted. One can see on the models a particularly strong packing of the methyl groups at the  $\gamma$  carbon atom with the methyl groups at the  $\alpha$ -carbon atom. At the same time both halves of the molecule may interact, which is reflected in an already marked increase in the rate of decomposition. By replacing the methyl group at the  $\gamma$ -carbon atom in both halves of *V* with the phenyl group (*VI*) the steric requirements increase again, which is reflected in an only slight increase in the rate of decomposition compared with the preceding compound. The incorporation of the two phenyl groups at the two  $\gamma$ -carbon atoms yields *VII*, the molecule of which is characterized by such considerable packing of all the methyl and phenyl groups that their freedom of rotation becomes almost impossible; moreover, there is a very strong interaction between both halves of the molecule. Here the effects of the B- and F- strain become fully operative. The rate of decomposition at 150°C is approximately 400 times higher compared to the unbranched compound *III*, and 1500 times higher compared to *I*.

The results (Tables I and II) show that the effect of the steric factors on the stability of azo compounds is considerable, though not so pronounced as the electronic effects. *I*, in which the steric effects are not reflected, is the stablest of the series; its temperature limits of decompositions are shifted highest. With gradually increasing steric requirements due to branching and to the size of the substituents the temperature limits decrease and the rate of decomposition increases. The highest rates of decomposition were reached by the branching of the basic chain on both  $\gamma$ -carbon atoms with respect to the azo group, with a simultaneous contribution of branching on the  $\alpha$ -carbon atoms; the size of the substituents at the  $\gamma$ -carbon atoms also has a favourable effect. For the latter three compounds, *V*, *VI*, *VII*, which fulfil the

above conditions, the rate of decomposition decreases by some 50°C compared to *I*, *II*, *III*, the activation energy decreases by 5–8 kcal/mol, and the rate increases by two or three orders of magnitude. The large agglomeration and packing of the groups gives rise to the B-strain, which along with the F-strain reduces the bond strength between the carbon and nitrogen atoms of the azo group and is the main cause of the increased thermal lability of these compounds.

TABLE I

Thermal Decomposition Rate Constants  $k_d \cdot 10^5$  ( $s^{-1}$ ) of Azo Compounds *I* to *VII* in Solution<sup>a</sup>

°C	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>
110	—	—	—	—	—	—	5.6
120	—	—	—	—	—	8.1	18.0
130	—	—	—	—	17.8	25.4	54.0
140	—	—	—	—	51.9	75.3	158.0
150	0.3 <sup>b</sup>	0.38 <sup>b</sup>	1.0 <sup>b</sup>	2.3	144.0	212.0	436.0 <sup>b</sup>
160	—	—	3.2	7.4	380.0	—	—
170	3.2	4.0	8.5	22.0	—	—	—
180	9.1	12.0	28.7	61.6	—	—	—
190	29.0	32.9	65.2	—	—	—	—
200	74.4	92.1	192.0	—	—	—	—

<sup>a</sup> Decompositions *I*–*III* were carried out in cetane<sup>13,14</sup>, *IV*–*VII* in toluene; <sup>b</sup> Recalculated to 150°C.

TABLE II

Activation Parameters of Decomposition of Azoalkanes

Com- pound	$E_a$ kcal/mol	$\log A$	$\Delta H^\ddagger$ kcal/mol	$\Delta G^\ddagger$ kcal/mol	$\Delta S^\ddagger$ (150°C) e.u.	Relative rate at 150°C
<i>I</i>	44.1 ± 0.9	17.26 ± 0.4	43.2 ± 0.9	35.7 ± 1.7	17.7 ± 1.8	1.0
<i>II</i>	43.4 ± 0.3	17.00 ± 0.16	42.5 ± 0.3	35.5 ± 0.6	16.5 ± 0.7	1.2
<i>III</i>	41.6 ± 1.1	16.50 ± 0.5	40.7 ± 1.1	34.7 ± 2.1	14.2 ± 2.3	3.3
<i>IV</i>	41.8 ± 0.2	16.96 ± 0.1	40.9 ± 0.2	34.0 ± 0.4 <sup>a</sup>	16.3 ± 0.5 <sup>a</sup>	7.7
<i>V</i>	36.3 ± 0.3	15.93 ± 0.2	35.5 ± 0.3	30.6 ± 0.7 <sup>b</sup>	11.6 ± 0.9 <sup>b</sup>	480.0
<i>VI</i>	35.9 ± 0.08	15.90 ± 0.04	35.0 ± 0.1	30.2 ± 0.2	11.4 ± 0.1	706.0
<i>VII</i>	35.0 ± 0.06	15.73 ± 0.03	34.2 ± 0.06	29.7 ± 0.1	10.7 ± 0.2	1 450.0

Ref.<sup>23</sup> gives for  $\Delta G^\ddagger$  and for  $\Delta S^\ddagger$ : <sup>a</sup> 34.3; 8; <sup>b</sup> 30.8; 4 (for 100°C).

## EXPERIMENTAL

## Syntheses of Compounds

2,2'-Azoisobutane (I), 2,2'-dimethyl-2,2'-azobutane (II), 2,2'-dimethyl-2,2'-azopentane (III) were obtained by oxidation of the respective amines with iodine pentafluoride<sup>13,14</sup>.

N-(1,1,2,2-Tetramethyl)propylurea (VIII). 23.6 g (0.39 mol) of urea was gradually dissolved with cooling and stirring in 41 ml of conc. sulphuric acid, after which 100 g (0.86 mol) of 2,3,3-trimethylbutane-2-ol<sup>15</sup> was added dropwise at 15–20°C. The mixture was stirred 24 h and left at room temperature for two days. The upper layer was separated, the lower layer was poured with stirring on 600 g of crushed ice, and pH was adjusted to 3 with a solution of sodium hydroxide. The precipitate was sucked off, washed with water and recrystallized from two litres of water. The yield was 19 g of N-(1,1,2,2-tetramethyl)propylurea monohydrate, m.p. 157–158°C. For C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O.H<sub>2</sub>O (176.2) calculated: 54.52% C, 11.44% H, 15.90% N; found: 54.60% C, 11.37% H, 15.90% N.

1,1,2,2-Tetramethylpropylamine (IX). 60 ml of ethylene glycol and 29 g (0.18 mol) of VIII were added to a 40% aqueous sodium hydroxide. The mixture was boiled 4 h under a reflux. The raw amine was distilled, the aqueous layer was shaken with ether. After that the ether was evaporated, both parts of the amine were joined and dried with potassium hydroxide. The product was distilled through a Vigrex column. The yield was 7.5 g (36%), b.p. 122–123°C (ref.<sup>16</sup> b.p. 120–121°C). Hydrochloride recrystallized from ethanol melts above 360°C (in a sealed capillary). (Ref.<sup>17</sup>, m.p. 305–306°C.) For C<sub>7</sub>H<sub>18</sub>ClN (151.6) calculated: 55.41% C, 11.96% H, 9.24% N; found: 55.55% C, 12.05% H, 9.25% N.

2,3,3,2',3',3'-Hexamethyl-2,2'-azobutane (IV). 47 ml pyridine was added to a solution of 13 ml of iodine pentafluoride in 250 ml of dichloromethane cooled to –20°C; after that, 30 g (0.26 mol) of IX in 150 ml of dichloromethane was added dropwise. The temperature was maintained between –10 and –20°C. The mixture was stirred for 3 h, then poured into 2 l of icy water. The organic layer was gradually extracted with dilute hydrochloric acid, solution of sodium thiosulphate, and water. After drying with anhydrous magnesium sulphate the solvent was evaporated on a rotary evaporator and the rest was dissolved in hexane. By strongly supercooling the solution, a yellow crystalline compound was obtained, which was repurified by crystallization from ethanol. The yield was 5.3 g (18.2%), m.p. 22–22.5°C.  $\lambda_{\max} = 376 \text{ nm}$ ,  $\epsilon = 18.9$  (For compound IV, which was synthesized by a different methods (ref.<sup>16,19</sup>), b.p. is 53–54°C/0.2 k Pa, 49–51°C / 26.7 Pa,  $\lambda_{\max}(\epsilon) = 376 \text{ nm}$ , 372 nm (18)). For C<sub>14</sub>H<sub>30</sub>N<sub>2</sub> (226.4) calculated: 74.27% C, 13.36% H, 12.37% N; found: 74.58% C, 13.41% H, 12.35% N.

2,4,4,2',4',4'-Hexamethyl-2,2'-azopentane (V) was prepared similarly to the preceding compound by the oxidation of 2-amino-2,4,4-trimethylpentane<sup>18</sup> with iodine pentafluoride. The yield was 15%. Colourless crystals from hexane, m.p. 21–22°C,  $\lambda_{\max} 372 \text{ nm}$ ,  $\epsilon 19.6$ . (For V prepared by other procedures other authors (ref.<sup>16–19</sup>) give b.p. 70–71°C/53.3 Pa, 86°C/13.4 Pa,  $\lambda_{\max}(\epsilon) 372 \text{ nm}$  (23)). NMR (CDCl<sub>3</sub> + HMDS):  $\tau$  9.05 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 8.88 (s, 12 H, C(CH<sub>3</sub>)<sub>2</sub>), 8.20 (s, 4 H, CH<sub>2</sub>). For C<sub>16</sub>H<sub>34</sub>N<sub>2</sub> (254.5) calculated: 75.52% C, 13.47% H, 11.01% N; found: 76.08% C, 13.67% H, 10.89% N.

2,4-Dimethyl-4-phenylpentane-2-ol (X) was prepared from 191 g (1.08 mol) of 4-methyl-4-phenylpentane-2-one<sup>20</sup> and methyl magnesium chloride (from 1.35 mol Mg). Yield 182 g (88%), m.p. 26.5–27.5°C, b.p. 106–108°C at 0.54 kPa (Ref.<sup>21</sup>, m.p. 24–26°C, b.p. 90–92°C at 12.7 kPa. For C<sub>13</sub>H<sub>20</sub>O (192.3) calculated: 81.20% C, 10.48% H; found: 80.97% C, 10.37% H.

*N-Formyl-1,1,3-trimethyl-3-phenylbutylamine* (XI). 11 g (0.2 mol) of sodium cyanide (content 95%) was gradually added to 50 ml of acetic acid with cooling and stirring, then a cool mixture of 27 ml of conc. sulphuric acid and 25 ml of acetic acid were added dropwise. All the time the temperature was maintained at about 20°C. The cooling bath was then removed, 37.5 g (0.195 mol) of *X* was added dropwise and the stirring was continued for another 2 h. The following day the mixture was poured into 100 ml of icy water, the oily layer was diluted with ether, separated, the aqueous layer was neutralized with a solution of sodium carbonate and extracted with ether. The ether fractions were combined, extracted with a solution of sodium carbonate and dried with anhydrous magnesium sulphate. The solvent was evaporated at reduced pressure and the rest was redistilled. Yield 29.5 g (70%), b.p. 174°C at 0.27 kPa. For C<sub>14</sub>H<sub>21</sub>NO (219.3) calculated: 76.67% C, 9.65% H, 6.39% N; found: 76.72% C, 9.60% H, 6.40% N.

*3-Phenyl-1,1,3-trimethylbutylamine* (XII). 29.5 g (0.13 mol) of XI was heated at 170°C for 24 h with a 23% aqueous solution of sodium hydroxide in an autoclave. The product was extracted with benzene and dried with potassium hydroxide. After that the solvent was removed and the amine was distilled through a concentric column (10 cm long). Yield 20 g (81%) of colourless liquid, b.p. 110–111°C at 0.94 kPa. NMR (CCl<sub>4</sub> + HMDS):  $\tau$  9.14 (s, 6 H, NH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>); 8.6 (s, 6 H, Ph.C(CH<sub>3</sub>)<sub>2</sub>); 8.14 (s, 2 H, CH<sub>2</sub>); 2.57–2.95 (m, 5 H, aromatic). For C<sub>13</sub>H<sub>21</sub>N (191.3) calculated: 81.61% C, 11.06% H, 7.32% N; found: 81.78% C, 11.10% H, 7.23% N.

*N,N'-Bis(1,1,3-trimethyl-3-phenylbutyl)sulphamide* (XIII). A solution of 9.57 g (0.05 mol) of 1,1,3-trimethyl-3-phenylbutylamine in 25 ml of hexane was cooled to -15°C. A solution of 1.7 g (0.0125 mol) of sulphuryl chloride in 20 ml of hexane was added dropwise with stirring. The temperature of the reaction mixture was maintained below 0°C. The stirring was continued at room temperature for another 30 min; after that, 50 ml water was added, the mixture was vigorously stirred and hexane was removed from the mixture on a rotary evaporator. The compound was sucked off and dried at reduced pressure over P<sub>2</sub>O<sub>5</sub>. The yield was 5.6 g of raw product, m.p. 77–78°C. The compound was repurified by dissolving in 20 ml of hot ethanol; 15 ml water was added to the hot filtered solution. On cooling the white precipitate was sucked off and dried over P<sub>2</sub>O<sub>5</sub>. Yield 4 g (36%), m.p. 79–80°C. For C<sub>26</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S (444.7) calculated: 70.22% C, 9.07% H, 6.3% N; found: 70.41% C, 9.40% H, 6.39% N.

*4,4'-Diphenyl-2,4,2',4'-tetramethyl-2,2'-azopentane* (VI). *a*) By the oxidative coupling of XII with iodine pentafluoride similarly to IV. Yield 3.1%. M.p. 63–74°C,  $\lambda_{\max}$  375 nm. For C<sub>26</sub>H<sub>38</sub>N<sub>2</sub> (378.6) calculated: 82.48% C, 10.12% H, 7.40% N; found: 82.42% C, 10.30% H, 7.41% N. *b*) By the oxidation of XIII with tert-butyl hypochlorite: A solution of 4 g (0.009 mol) of XIII in 20 ml of anhydrous benzene was added dropwise with stirring to a suspension of 0.44 g (0.018 mol) of sodium hydride in 5 ml of dry benzene. The reaction mixture was stirred for 5 h, 15 ml of hexane was added, the mixture was cooled to -5°C and a solution of 2 g (0.018 mol) of tert-butyl hypochlorite in 10 ml of hexane was added dropwise, with the temperature maintained between -5 and 0°C. The mixture was stirred at room temperature for another 14 h. The unreacted sodium hydride was removed by cautious dropwise addition of water with cooling, the aqueous layer was separated and extracted with ether. The organic fractions were joined and dried with anhydrous magnesium sulphate. 3 g of white crystalline compound was obtained after the evaporation of solvent. The product was recrystallized from a methanol-ether mixture. Yield 2.5 g (73.5%), m.p. 63–64°C,  $\lambda_{\max}$  374 nm,  $\epsilon = 23.8$ ; NMR (CCl<sub>4</sub> + HMDS):  $\tau$  9.26 (s, 2 H, N.C(CH<sub>3</sub>)<sub>2</sub>); 8.74 (s, 12 H, Ph.C(CH<sub>3</sub>)<sub>2</sub>); 7.78 (s, 4 H, CH<sub>2</sub>); 2.48–2.93 (m, 10 H, aromatic). For C<sub>26</sub>H<sub>38</sub>N<sub>2</sub> (378.6) calculated: 82.48% C, 10.12% H, 7.40% N; found: 82.50% C, 10.17% H, 7.61% N.

*4,4-Diphenylpentane-2-one* (XIV). A solution of 32 g (0.2 mol) of 4-phenylpent-3-ene-2-one<sup>22</sup>

in 30 ml of dry benzene was added dropwise during 3 h to 36 g (0.26 mol) of anhydrous aluminium chloride in 50 ml of dry benzene cooled to 5°C. The temperature was maintained between 5 and 10°C. The mixture was stirred at this temperature for another 3 h, and after that was poured on 250 g of crushed ice. The product was extracted with ether, the ether solution was filtered with decolorizing carbon and dried with anhydrous magnesium sulphate. Evaporation of the solvent yielded 37 g (78%) of the product in the form of yellow oil having sufficient purity for further treatment. For analysis, 1 g of raw product was dissolved in light petroleum and cooled for a long time, which yielded colourless crystals, m.p. 33–35°C. For  $C_{17}H_{18}O$  (238.3), calculated: 85.67% C, 7.61% H; found: 85.76% C, 7.86% H.

4,4-Diphenyl-2-methylpentane-2-ol (XV). A solution of 47.7 g (0.2 mol) *XIV* in 400 ml of dry ether was added with stirring to methylmagnesium bromide prepared from 5.6 g (0.23 mol) magnesium in 300 ml of dry ether. The mixture was heated to boil for 1 h. On cooling, a solution of 20 g of ammonium chloride in 80 ml of water was added dropwise. The ether layer was separated, the salt was washed twice with 200 ml of ether, the ether fractions were combined and dried with anhydrous magnesium sulphate. Evaporation of ether and distillation of the residue yielded 46 g (91%) of colourless oil, b.p. 165–166°C/0.4 kPa. For  $C_{18}H_{22}O$  (254.4) calculated: 84.99% C, 8.72% H; found: 84.90% C, 8.77% H.

N-Formyl-3,3-diphenyl-1,1-dimethylbutylamine (XVI). 2.8 g (0.057 mol) of sodium cyanide was gradually added with stirring to 13 ml of acetic acid cooled with icy water. The temperature was maintained within 10–20°C. After that a cooled mixture of 6 ml of acetic acid and 10 ml of conc. sulphuric acid was added to the mixture so that the temperature did not exceed 20°C. On removal of the cooling bath a solution of 11.75 g (0.046 mol) of *XV* in 11 ml of acetic acid was added dropwise. The mixture was stirred at room temperature for 8 h, left to stand overnight and then poured into 40 ml of icy water. pH was adjusted to 9 by means of a solution of sodium carbonate and the product was extracted with ether. Evaporation of the solvent and crystallization from ethanol gave 4.5 g of white crystalline compound, m.p. 112–113°C. An ether-hexane mixture (1 : 1) was added to concentrated mother liquors, and another 1.5 g of the compound (m.p. 110–111°C) was obtained on cooling. The total yield was 6 g (46%). For  $C_{19}H_{23}NO$  (281.4) calculated: 81.10% C, 8.24% H, 4.98% N; found: 81.01% C, 8.39% H, 4.72% N.

1,1-Dimethyl-3,3-diphenylbutylamine (XVII). 21 g (0.075 mol) of *XVI* was hydrolyzed in an autoclave at 175°C for 21 h with a 20% solution of sodium hydroxide. The product was extracted with ether. On drying with potassium hydroxide and evaporation of the solvent the remaining oil was redistilled. The yield was 13.5 g (71.5%) of amine, b.p. 152–154°C/0.14 kPa. NMR ( $CCl_4 + HMDS$ ):  $\tau$  9.11 (s, 6 H,  $NH_2.C(CH_3)_2$ ), 8.20 (s, 3 H,  $Ph_2.C.CH_3$ ), 7.63 (s, 2 H,  $CH_2$ ), 2.63–3.00 (m, 10 H, aromatic). For  $C_{18}H_{23}N$  (253.4) calculated: 85.32% C, 9.15% H, 5.53% N; found: 85.41% C, 9.08% H, 5.06% N.

4,4-Diphenylpentane-2-one-azine (XVIII). 3.8 g (0.075 mol) of hydrazine hydrate and 0.5 ml of ether saturated with hydrogen chloride was added to a solution of 36 g (0.15 mol) of raw *XIV* in 350 ml of ethanol. The mixture was heated to boil for 5 h. Evaporation of the solvent yielded 37 g of yellowish crystalline compound which was recrystallized from ethyl acetate. The yield was 20 g (56%) of white crystalline compound, m.p. 157–158°C. For  $C_{34}H_{36}N_2$  (472.7) calculated: 86.40% C, 7.68% H, 5.93% N; found: 86.04% C, 7.70% H, 6.36% N.

2,2'-Dichloro-4,4,4',4'-tetraphenyl-2,2'-azopentane (XIX). Chlorine was introduced into a solution of 19 g (0.04 mol) *XVIII* in 200 ml of methylene chloride cooled to –40°C until the solution became intensively yellow. The solvent was evaporated on a rotary evaporator at room temperature. 80 ml of light petroleum was added to the remaining yellow compound and the solution was cooled with dry ice. The precipitate was sucked off and dried *in vacuo* over  $P_2O_5$ . Yield 15.5 g

(70·9%), m.p. 128—136°C. For analysis, a sample of the compound was recrystallized from the mixture methylenechloride—light petroleum, m.p. 132—136°C,  $\lambda_{\max}$  363 nm. For  $C_{34}H_{36}N_2Cl_2$  (543·6) calculated: 75·12% C, 6·67% H, 5·15% N; found: 75·24% C, 7·07% H, 5·07% N.

2,2'-Dimethyl-4,4,4',4'-tetraphenyl-2,2'-azopentane (VII). a) By the oxidation of *XVII* with iodine pentafluoride as described for *IV*. The product was repurified by column chromatography on neutral aluminium oxide (benzene as eluent). Yield 9%, m.p. 131—134°C,  $\lambda_{\max}$  375 nm. For  $C_{36}H_{42}N_2$  (502·7) calculated: 86·01% C, 8·42% H, 5·57% N; found: 85·92% C, 8·53% H, 5·78% N. b) A solution of 15·1 g (0·028 mol) *XIX* in 150 ml of dry benzene was added dropwise with stirring to a suspension of methylmagnesium bromide prepared from 4·8 g (0·197 mol) magnesium in 250 ml of dry ether. The reaction mixture was stirred at room temperature for 3 h, and a saturated solution of ammonium chloride was added with cooling and intensive stirring. The salt that precipitated from the solution was washed with benzene, the organic fractions were joined and dried with anhydrous magnesium sulphate. Evaporation of the solvent yielded 14·5 g of raw product which was dissolved in a mixture of 100 ml of methylene chloride and 30 ml of methanol and filtered with decolorizing carbon. Strong supercooling yielded a white compound, m.p. 127—133°C, which was repurified by column chromatography on neutral aluminium oxide. Benzene was used as eluent. Yield 7 g (50%), m.p. 131—133°C,  $\lambda_{\max}$  374 nm,  $\epsilon$  25·9; NMR ( $CDCl_3$  + HMDS),  $\tau$  9·15 (s, 12 H,  $N.C(CH_3)_2$ ); 8·34 (s, 6 H,  $Ph_2.C.CH_3$ ); 7·15 (s, 4 H,  $CH_2$ ); 2·15—2·55 (m, 20 H, aromatic). For  $C_{36}H_{42}N_2$  (502·7) calculated: 86·01% C, 8·42% H, 5·57% N; found: 86·64% C, 8·44% H, 5·53% N.

#### Kinetics of Thermal Decomposition of Azo Compounds

The decomposition of the azo compounds investigated in this work was carried out in toluene solution in sealed ampoules by a procedure described earlier<sup>13</sup>. Kinetic measurements were carried out at four temperatures; concentration changes of the azo compounds with time were determined by UV spectroscopy on a Cary 14 apparatus. The rate constants were calculated from the dependence of  $\log(D_0/D)$  on time. In all cases perfect linear dependences were obtained which fulfilled the equation for first-order reactions. The values of the activation energy and pre-exponential factor were determined by the least squares method.

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