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Aliphatic Azo Compounds, XV[1]

cis- and *trans*-Tetracyclopropyl- and Tetra-*tert*-butylazomethanes

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The products and the kinetics of the thermolysis of the title compounds **3** and **5** were investigated. Like the *trans*-isomers, the *cis*-azo compounds also undergo homolytic decomposition without accompanying *cis-trans*-isomerization. The observed structure-reactivity relationships are discussed. On irradiation of *trans*-tetra-*tert*-butylazomethane (*trans*-**5**) at 60–120°C in benzene or chlorobenzene an almost quantitative yield of 1,1,2,2-tetra-*tert*-butylethane is obtained.

Aliphatische Azoverbindungen, XV[1]

***cis*- und *trans*-Tetracyclopropyl- und Tetra-*tert*-butylazomethan**

Die Produkte und die Kinetik der Thermolysen der Titelverbindungen **3** und **5** wurden untersucht. Wie die *trans*-Isomeren, so zerfallen auch die *cis*-Azoverbindungen in Radikale ohne begleitende *cis-trans*-Isomerisierung. Der Einfluß der Strukturvariation auf die Reaktivität wird diskutiert. Durch Bestrahlen von *trans*-Tetra-*tert*-butylazomethan (*trans*-**5**) bei 60–120°C in Benzol oder Chlorbenzol läßt sich fast quantitativ 1,1,2,2-Tetra-*tert*-butylethan darstellen.

The *cis-trans*-isomerizations and the thermolysis reactions of tertiary azoalkanes have been investigated much more thoroughly than those of secondary ones **1**[2]. This is due to an additional complicating side reaction of the latter, the tautomerization to hydrazones **2**[3].

$R_2CH-N=N-CHR_2$ **1** $R_2CH-NH-N=CR_2$ **2**

Through our attempts to prepare 1,1,2,2-tetra-*tert*-butylethane[4] and 1,1,2,2-tetracyclopropylethane[5,6] the title azo compounds became available. The observation that they were not very sensitive to tautomerization stimulated our interest in the investigation of their thermal decomposition reactions.

Synthesis

A mixture of *cis*- and *trans*-1,1,1′,1′-tetracyclopropylazomethane (**3**) was obtained[6] from dicyclopropyl ketone via the azine, followed by reduction to the hydrazine and subsequent air oxidation.

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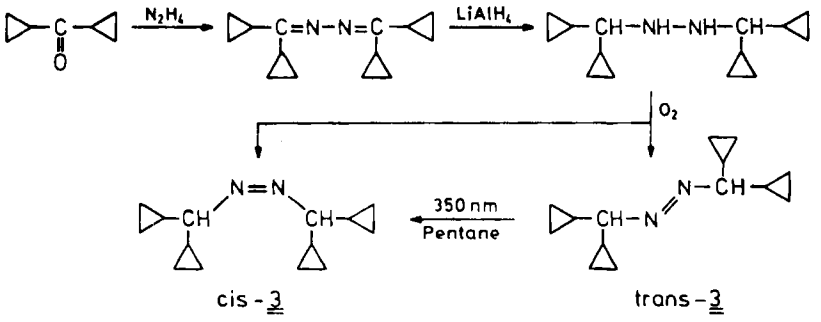
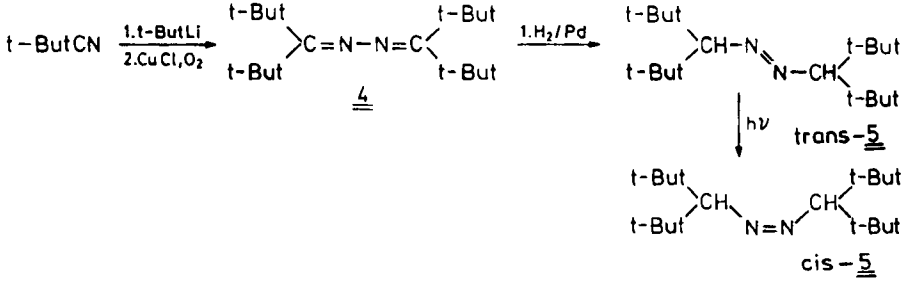


The two isomers were separated by crystallization from pentane. Alternatively, *trans*-**3** was isomerized to *cis*-**3** by 350 nm irradiation in petrol ether[7].

The preparation of *cis*- and *trans*-1,1,1′,1′-tetra-*tert*-butylazomethane (**5**) was more cumbersome[8]. The ketimin of di-*tert*-butyl ketone was obtained from pivalonitrile and *tert*-butyllithium and oxidized to the azine **4** following the general procedure of *Kauffmann* et al.[9]. This synthesis of **4** proved to be superior to a procedure in the literature[10] via the Cu^+-catalyzed decomposition of di-*tert*-butyl diazomethane[10]. **4** was hydrogenated to the azo compound *trans*-**5**.



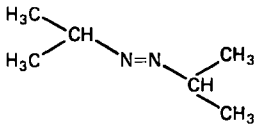
cis-**5** was obtained from *trans*-**5** by 360 nm irradiation in toluene at 0 °C and separation by chromatography over Al_2O_3 at the same temperature.

By irradiating *trans*-**5** in benzene or chlorbenzene between 60 and 120 °C an almost quantitative yield of 1,1,2,2-tetra-*tert*-butylethane was obtained. This reaction is probably proceeding via thermal decomposition of photochemically generated *cis*-**5** followed by the recombination of intermediate di-*tert*-butylmethyl radicals. This is the most efficient synthesis of tetra-*tert*-butylethane[4,11] and a convenient source for the photochemical generation of di-*tert*-butylmethyl radicals[12].

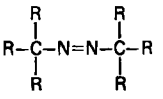
The n-π^* absorptions of *trans*-**3** (TCAM) and *trans*-azoisopropane (*trans*-**6**) (AIP: 1,1′-dimethylazoethane) (cf. Table 1) are almost identical, while *trans*-**5** (TBAM) absorbs at about 25 nm longer wavelength with a somewhat higher ε. This corresponds to the situation found previously for tertiary azoalkanes, namely, that due to bulky groups λ_{max} is generally increased[2,13].

A similar situation is found for the *cis*-isomers in this paper. *cis*-**3** and *cis*-**6** absorb at 383 and 380 nm, respectively, but the more bulky *cis*-**5** absorbs at 411 nm. According to an ab

initio analysis of *Baird* et al.[17] this is due to the increase of the NNC bond angle. From a correlation between the NNC angle in *cis*-azoalkanes (obtained by EFF calculations[7]) and λ_{max} for a series of *cis*-azoalkanes[7], the NNC angle in *cis*-**5** is estimated to be increased to 125° (i.e. only 2° larger than in *cis*-**6**). Consequently, the response of the NNC angle in secondary *cis*-azoalkanes **1** to the bulk of the groups R is much smaller than in the tertiary series **7**[7].



trans–**6**



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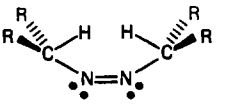

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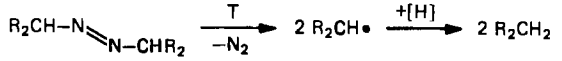
Apparently conformation **8**, in which the two small hydrogen atoms bound at the central carbons are in opposition, is the preferred one.

Thermal Decompositions

trans-**3** and *trans*-**5** decompose at about 200–250 °C with homolytic bond cleavage into dicyclopropylmethyl and di-*tert*-butylmethyl radicals, respectively. From *trans*-**3** thermolysis in tetraline a 75% yield of dicyclopropylmethane or one of its homoallylic isomers ($C_7H_{12}^+$ by MS) was analyzed by gc. Likewise a 93% yield of di-*tert*-butylmethane was found when *trans*-**5** was decomposed in 9,10-dihydroanthracene.



The activation enthalpies ΔG^* for these thermolysis reactions are 4 and 6 kcal · mol^{-1}, respectively, lower than for the decomposition of *trans*-AIP (**6**) as seen from Table 1. ΔS^* is very similar throughout. For **3** the decrease in ΔG^* is due to the cyclopropyl stabilization of the dicyclopropylmethyl radical which has been estimated independently to be about 2.4 kcal · mol^{-1} [18,19] per radical. The decreased thermal stability of *trans*-**5** as compared to *trans*-**6** can be ascribed to the release of B-strain as it was observed previously in the series of tertiary azoalkanes **7**[2,20].

The same effects of structure variation on rates are again found in the series of *cis*-azoalkanes (see Table 1) in which steric effects, as expected, are more pronounced. The difference in ΔH^* of the decomposition of *cis*-**6** and *cis*-**3** is remarkably small and accounted for by the radical stabilization effect. In accordance with the preferred conformation **8**, which allows for only small steric interaction between the non-geminal R groups, no steric effect is found. The difference in reactivity between AIP (**6**) and azo-*tert*-butane (1,1,1′,1′-tetramethylazoethane, **7**, R = CH_3) for the same reaction is smaller in the *trans*-series (ΔT(decomp.) = 30 °C) than in the *cis*-series (ΔT(decomp.) = 170 °C)[2]. ΔH^* for the decomposition of *cis*-**5**, though, is about 12 kcal · mol^{-1} smaller than for *cis*-**6**, which must be due to release of strain in *cis*-**5**.

Table 1. Spectra and kinetics of thermal decomposition of *cis*- and *trans*-azo compounds **3**, **5** and **6**

	AIP[a] (6)	TCAM[a] (3)	TBAM[a] (5)
trans			
λ_{max} (ε)	357 (17)[13]	361 (19)	385 (26)
Solvent	gas	cyclohexane	*n*-hexane
Kinetic method		DSC (tetraline)[b]	DSC (DHA)[c,d]
$\Delta G^{\neq}$ (300 °C) [kcal · mol^{-1}]	38.6[14]	34.6	32.2
$\Delta H^{\neq}$ [kcal · mol^{-1}]	46.7[14]	44.7 ± 0.4	43.1 ± 0.3
$\Delta S^{\neq}$ [e.u.]	14.1[14]	17.7 ± 0.8	19.1 ± 0.7
$\Delta G^{\neq}$ (200 °C) [kcal · mol^{-1}]	40.0	36.3	34.1
cis			
λ_{max} (ε)	380 (140)[15]	383 (76)	411
Solvent	isooctane	mesitylene	toluene
Kinetic method	UV (isooctane)	DSC (mesitylene)[e] [UV (mesitylene)]	DSC (thiophenol)[f,g]
$\Delta G^{\neq}$ (50 °C) [kcal · mol^{-1}]	33.7[2]	29.3 [29.2]	21.9
$\Delta H^{\neq}$ [kcal · mol^{-1}]	39.8 ± 1.8[2]	34.4 ± 0.1 [34.4 ± 0.5]	27.6 ± 0.1
$\Delta S^{\neq}$ [e.u.]	18.9 ± 4.1[2]	15.7 ± 0.2 [16.1 ± 1.4]	17.8 ± 0.8

[a] AIP = 1,1′-dimethylazoethane (azoisopropane), TCAM = *sym*-tetracyclopropylazomethane, TBAM = *sym*-tetra-*tert*-butylazomethane. — [b] Exothermic peak between T = 200 and 260 °C with the maximum at T_m = 240 °C and a shape ratio (area behind T_m over area befor T_m) f = 0.65 ± 0.01 (first order reaction[26]). — [c] Obtained from the simulated peak for the first oder reaction (f = 0.63) fitted to the measured exothermic peak (700 mcal) at T = 170–235 °C, f = 0.85. — [d] DHA = 9,10-dihydroanthracene. — [e] One DSC run only. — [f] For comparison the rate was measured in toluene at 30 ± 1 °C by UV: k_1 = 1.344 ± 0.01 · 10^{-3} s^{-1}; from the DSC measurements k_1 (30.0 °C) = 0.593 · 10^{-3} s^{-1} is obtained. Taking into account the solvent effect of the decomposition of *cis*-azo compounds[16] the agreement is satisfactory. — [g] Obtained from the simulated peak (first order, f = 0.63) fitted to the measured exothermic peak (100 mcal) at T = 25–65 °C, f = 0.70.

It has been shown[7] that only part of the strain in *cis*-azoalkanes is recognized in the response of λ_{max} or the corresponding increase of the NNC angle, which was rather moderate for *cis*-**5** (see above). In addition *cis*-**5** apparently responds to strain quite strongly by deformation of the alkyl groups due to van der Waals interactions between non-geminal *tert*-butyl groups (F-strain).

Of course tertiary *cis*-azoalkanes respond to the increase of the bulkiness of the groups much more strongly[2,21] than secondary ones, because no favorable ground state conformation like **8** is available.

As shown by product analyses (see Exp. Part), *cis*-**3** and *cis*-**5** decompose cleanly into radicals at elevated temperatures. In contrast, *cis*-**6** partially isomerizes to *trans*-**6** in a competing reaction[15]. If it is assumed that the heat of isomerization

is not very different for **3** and **6** (−8 to −10 kcal·mol^{-1})[2,7] then the exclusive homolytic decomposition of *cis*-**3** can be understood to be due to the already mentioned better stabilization of dicyclopropylmethyl radicals than isopropyl radicals. This is evidence in favor of an inversion mechanism for the *cis-trans*-isomerization over the radical pair mechanism, suggested in the recent literature (for a discussion see ref.[1]). The exclusive homolytic decomposition of *cis*-**5** without competing isomerization is, accordingly, due to greater steric acceleration of the decomposition pathway[21] as compared to the *cis-trans*-isomerization[2,7,22], which, again is in favor of the inversion mechanism for the isomerization[1].

Thanks are due to *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* for generous support of this work and to Prof. *J. W. Timberlake*, New Orleans, for providing the procedure for the synthesis of **3**.

Experimental Part

The instrumentation for the spectroscopic, chromatographic and thermochemical work was listed recently[23].

Syntheses

cis- and trans-Bis(dicyclopropylmethyl)diazene = cis- and trans-1,1,1',1'-Tetracyclopropylazomethane (**3**)[6]: 9.0 g (42 mmol) of dicyclopropyl ketazine[24] in 80 ml of ether was slowly added at −78°C under N_2 to a suspension of 8.0 g (0.20 mol) of $LiAlH_4$ in 200 ml of ether. After completion of the addition the solution was heated under reflux for 10 h. Excess hydride was destroyed by the addition of ethyl acetate and the precipitated aluminium salts were removed by filtration. For the oxidation of the hydrazine to the azo compound oxygen was introduced into the solution for 5 h through a glass frit. Finally the solution was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The remaining yellow oil was dissolved in pentane for crystallization. 2.5 g (27%) of *cis*-**3** crystallized first as large yellow needles, m.p. 117−118°C from petrol ether (30−50°C) (Lit.[6] 110−111°C). − UV: λ_{max} (ε) = 384 nm (62), in cyclohexane; 383 nm (76), in mesitylene. − ^{1}H-NMR ($CDCl_3$): δ = 0.00−0.76 (m; 16H, CH_2), 1.00−1.45 (m; 4H, CH), 2.80 (t; *J* = 12 Hz; 2H, CHN=NCH). − ^{13}C-NMR ($CDCl_3$): δ = 2.04 (t; CH_2), 2.43 (t; CH_2), 13.97 (d; CH), 73.06 (d; CH−N).

From the mother liquor 3.1 g (34%) of *trans*-**3** separated on further concentration. Fine white needles with m.p. 39−40°C (Lit.[6] 39−40°C). − UV (cyclohexane): λ_{max} (ε) = 361 nm (19). − ^{1}H-NMR (HMDS): δ = 0−0.64 (m; 16H), 0.89−1.33 (m; 4H), 1.93 (t; 2H, *J* = 16 Hz).

cis-**3** was also obtained when an 0.05 M solution of *trans*-**3** was irradiated in petrol ether (30−50°C) at 25°C under N_2 with 350 nm light in a Rayonett or a Gräntzel photoreactor till the bright yellow colour of *cis*-**3** appeared. The separation from *trans*-**3** was achieved by column chromatography at room temperature and subsequent recrystallization from pentane at −30°C.

cis- and trans-Bis(1-tert-butyl-2,2-dimethylpropyl)diazene = cis- and trans-Tetra-tert-butylazomethane (**5**)

Di-tert-butyl Ketone Azine (**4**)[9]: Under dry N_2 0.1 mol of *tert*-butyllithium in 70 ml of ether was cooled to −10°C in a 250 ml three-necked flask provided with an intensive condenser, dropping funnel, thermometer, and a magnetic stirring device. After slowly adding

8.3 g (0.10 mol) of pivalonitrile the temperature was raised and kept at 25°C for 3 h. The solution was then cooled again to −10°C and 0.50 g (5.0 mmol) of CuCl and 50 ml of anhydrous tetrahydrofuran were added. The temperature rose within 5 min to 8°C and then returned to −10°C within 20 min. Stirring was continued for 12 h at 25°C under a slow stream of N_2. Finally at 15°C a stream of O_2 was introduced for about 2 h. The solution turned dark brown and CuO precipitated. When the temperature no longer increased the solution was hydrolyzed by addition of 200 ml of ice water. The blue aqueous phase was extracted five times with 100 ml of ether and the extracts were washed and dried over $MgSO_4$. The solvent was removed by distillation and the light yellow crystalline residue was chromatographed at 0°C in petrol ether over silica gel. The fractions containing the ketazine (DC control) were combined and recrystallized from ethanol. 11.3 g (41%) of fine white needles; m.p. 70°C (Lit.[10] 67.5–69.5°C).

trans-**5**: 7.1 g (25.7 mmol) of ketazine **4** was hydrogenated in 900 ml of glacial acetic acid with 200 mg of PtO_2 catalyst at room temperature and at atmospheric pressure. The hydrogen uptake stopped when 1.3 l was absorbed. The catalyst was removed by filtration and the solution concentrated in vacuo. A white crystalline material was obtained, which was refluxed for 1 h with 10% NaOH and then extracted several times with ether. The ether was washed with water, dried over $MgSO_4$, and distilled off through a vigreux column. The remaining 2.9 g of *trans*-**5** was dissolved in petrol ether and purified by chromatography over neutral Al_2O_3 (activity I) in the same solvent. The yellow fractions were collected, concentrated, and their residues were crystallized from pentane. Large, light yellow platelets melting at 61–63°C were obtained. – UV (*n*-hexane): λ_{max} (lg ε) = 384.5 nm (1.413). – ^{1}H-NMR (CCl_4, HMDS): δ = 0.98 (s; 36H, $C(CH_3)_3$), 2.5 (s; 2H, CH). – MS (CI Methane): *m/z* = 284 (23.2%, $M^+ + 2$), 283 (100, $M^+ + 1$), 282 (5.6, M^+), 228 (12.1), 227 (62.2), 127 (6.3, $((CH_3)_3C)_2CH^+$), 71 (25.8, $(CH_3)_3CCH_2^+$), 57 (36.6, $(CH_3)_3C^+$).

$C_{18}H_{38}N_2$ (282.3) Calcd. C 76.51 H 13.57 N 9.91 Found C 76.62 H 14.06 N 10.13

Table 2. Product analyses of thermolysis reactions of azo compounds **3** and **5**

Compound Solvent	T [°C]	Product	%	Remarks
trans-**3** tetraline	240	C_7H_{12} [a]	75	MS: *m/z* = 90 (9, M^+), 81 (42, $M^+ - CH_3$), 67 (42), 55 (42), 54 (60), 53 (74), 41 (100)
cis-**3** [b] mesitylene	105	C_7H_{12} [a] $C_{16}H_{22}$ [c]	60 ± 10 ≈30	MS: as above MS: *m/z* = 119 (mesityl$^+$, 3) 95 (M − mesityl$^+$, 57) 67 (73), 55 (30), 53 (17)
cis-**5** benzene	80	$C_{18}H_{38}$ *trans*-**5**	90 10	1,1,2,2-tetra-*tert*-butylethane [4] presumably formed by photoisomerization of *cis*-**5** during manipulation
trans-**5** 9,10-dihydroanthracene	240	C_9H_{20}	93	di-*tert*-butylmethane (GC-MS)

[a] Presumably dicyclopropylmethane or a homoallylic isomer. – [b] No *trans*-**3** was detectable as thermolysis product by GC and UV. – [c] Tentatively assigned to a coupling product of dicyclopropylmethyl and mesityl radicals.

cis-**5**: 100 mg of *trans*-**5** was irradiated for 2 h (360 nm) in 15 ml of toluene at 0°C. Afterwards the solution was chromatographed in a cooled column (10 cm × 2 cm) with basic Al_2O_3 (activity I). First *trans*-**5** was eluted with 20 ml of toluene and finally *cis*-**5** with methanol. When the methanol was evaporated at −10°C in vacuo 10 mg of solid, intensely yellow *cis*-**5** was obtained which was stored in the dark at −20°C. – UV (toluene): λ_{max} = 411 nm.

Thermolysis

Products: For product analyses the completely reacted solutions from the kinetic measurements were used. The products were identified by comparison of their retention times with those of authentic samples and by GC-MS coupling experiments. Quantitative product compositions were obtained by GC with internal standard[25]. For the results see Table 2.

Kinetics

a) *By Differential Scanning Calorimetry (DSC)*[23]: 1−4 mg of the azo compound was weighed into a pressure tight pan of the DSC instrument, dissolved in 8−10 µl of solvent, and the pan was closed by a screw connection. For *cis*-azo compounds the manipulations were done under red light. The reference pan contained the same amount of solvent. The temperature scale of the calorimeter was checked carefully, using the melting points of *n*-octadecane (28.25°C) and indium (156.6°C), respectively, as reference points. The heat rate was 5 K/min, the sensitivity 0.5 mcal/sec. The DSC curves were recorded online by a Commodore 8032 computer. For the evaluation of the data a dialogue was used providing a base line correction[7] and calculating the order of the reaction[26]. The activation parameters were partly obtained by fitting to a simulated peak. The data are mean values of generally 2−5 kinetic runs[7,12]. To the solutions of *cis*-**3** a small amount of DABCO was added to prevent acid catalysis[22].

b) *UV Method:* The method was described previously[22]. The rates of decomposition of *cis*-**3** were followed at 6 temperatures between 92.2 and 115.0°C in mesitylene following the extinction at 383 nm.

Photodecomposition of trans-1,1,1′,1′-Tetra-tert-butylazomethane (*trans*-**5**): 20 mg of *trans*-**5** dissolved in 0.3 ml of C_6D_6 was sealed in a thick NMR tube (borosilicate glass) under N_2. The tube was then irradiated for 2 h at 80°C with a Philips 1000 W SP lamp, using a selective Schott mirror 322. By ^{1}H NMR analysis 5.5% of *trans*-**5**, 93.2% of 1,1,2,2-tetra-*tert*-butylethane[4], and 3% of non identified products were analyzed. – ^{1}H NMR (250 MHz, C_6D_6): δ = 1.17 (s; 9H, $C(CH_3)_3$), 1.30 (s; 9H, $C(CH_3)_3$), 2.34 (s; 2H, CH).

CAS Registry Numbers

(*E*)-**3**: 100515-66-0 / (*Z*)-**3**: 100515-65-9 / **4**: 61833-36-1 / (*E*)-**5**: 100515-68-2 / (*Z*)-**5**: 100515-67-1 / $NCCMe_3$: 630-18-2 / dicyclopropyl ketazine: 15813-18-0

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