PREPARATION AND THERMAL DECOMPOSITION OF BRANCHED AZO ESTERS*

M. PROCHÁZKA

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

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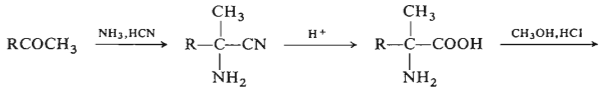
Oxidative coupling of α-amino esters was used to prepare several tertiary azo compounds containing the methoxycarbonyl group on the α-carbon atom with respect to the azo group. The kinetics of the thermal decomposition of these azo compounds in solution were measured, and the effects of structure on the kinetic parameters were studied.

The preparation and investigation of the thermal decomposition of strongly branched azo alkanes from the viewpoint of steric effects have been dealt with in a preceding paper[1]. In order to investigate simultaneously steric and electronic effects, we prepared azo esters of the general formula $R(CH_3)(COOCH_3)C{-}N{=}N{-}C(COOCH_3).(CH_3)R$ having a branched skeleton similar to the azo alkanes studied earlier[1]. In addition to the aims outlined above, we also attempted to employ the steric and resonance effect on the stability of the azo compounds in order to obtain new low-temperature initiators of radical polymerization. *I* was prepared according to Thiele and Heuser[2]. *II* to *V* could not be obtained by this procedure, because hydrogen cyanide was split off in the hydrolysis of hydrazonitriles. These compounds were therefore prepared by oxidizing the respective amino esters with iodine pentafluoride. Amino esters were obtained by modified Strecker's synthesis from the respective ketones, followed by hydrolysis and esterification.



I, R = CH_3
II, R = $CH_3C(CH_3)_2$
III, R = $CH_3C(CH_3)_2CH_2$
IV, R = $C_6H_5C(CH_3)_2CH_2$

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α-Aminonitriles were hydrolyzed with hydrochloric acid; only 2,3,3-trimethylbutyronitrile could not be hydrolyzed in this way for steric reasons. Concentrated sulphuric acid was used in this case, and the hydrolysis of the transitionally formed amide was completed with dilute acid. The yields of azo esters by oxidative coupling of α-amino esters varied from 27% to 31%. The compounds were identified by elemental analysis and by ^{1}H-NMR and UV spectroscopy.

EXPERIMENTAL

Synthesis of Compounds

2-Amino-2,3,3-trimethylbutyronitrile (*IX*) was prepared according to Gulewitsch and Wasmus[3] with the following modification. To a mixture of 130 ml methanol and 90 ml aqueous ammonia saturated at −10° with ammonia, 135 ml (3·5 mol) hydrogen cyanide was added with stirring, and after that 250 g (2·5 mol) 3,3-dimethyl-2-butanone was also added. Ammonia was introduced for another 30 min. The mixture was stirred at 0°C for 2 h and left three days at room temperature. Crystals precipitated on cooling were separated by filtration. Further fraction was obtained by concentrating mother liquors. The yield of the raw product was 230 g. By crystallization from 700 ml hexane, 190 g (60%) nitrile was obtained. M.p. of hydrochloride was 154—155°C (in a sealed capillary).

2-*Amino*-2,3,3-*trimethylbutyric acid* (X). 90 g (0·7) mol *IX* was added in parts with stirring to 150 ml (2·8 mol) of conc. sulphuric acid at 20°C at utmost. The mixture was left at room temperature for three days, diluted with 100 ml of water, stirred one hour, heated under a reflux in an aqueous bath for 70 h and to 120—130°C for 22 h. The cooled mixture was poured out on 100 g ice, and pH was adjusted to 6·5 by adding aqueous ammonia. The precipitate was filtered by suction, dried, and extracted with boiling methanol. The methanolic solution was evaporated, the residue was dissolved in 600 ml of water, and the solution was refiltered with activ carbon. 45 g of barium carbonate was added to the filtrate, and the mixture was stirred 12 h. The precipitated barium sulphate containing carbonate in excess was filtered by suction, and the filtrate was concentrated at reduced pressure. The product that separated was filtered by suction, recrystallized from 50% ethanol, and dried *in vacuo* at 110°C for three days. Yield 40 g (39%), m.p. 309—312°C. For $C_7H_{15}NO_2$ (145·2) calculated: 57·90% C, 10·41% H; 9·65% N; found: 58·05% C, 10·31% H, 9·95% N.

Methyl ester of 2-*amino*-2,3,3-*trimethylbutyric acid* (XI). A suspension (0·27 mol) of *X* in 400 ml methanol was saturated with hydrogen chloride under cooling and stirring and after that heated to boil for 5 h. 150 ml benzene was added to the mixture and evaporated at reduced pressure. The whole process was repeated twice. The residue was alkalized with a soda solution, and the product was extracted with ether. After that the ether solution was dried with anhydrous magnesium sulphate; the solvent was removed by distillation, and methyl ester was redistilled through a 10 cm Vigreux column. Yield 22 g (50%). B.p. 74—75°C/2 kPA. For $C_8H_{17}NO_2$ (159·2) calculated: 60·35% C, 10·75% H, 8·80% N; found: 60·20% C, 10·91% H, 8·49% N.

2,2′-*Azo-bis*(*methyl* 2,3,3-*trimethylbutyrate*) (II). To a mixture of 220 ml dichloromethane, 33 ml pyridine and 9 ml iodine pentafluoride[4], a solution of 20 g (0·178 mol) *XI* in 50 ml dichloromethane was added at −40°C with stirring during 30 min. The mixture was stirred at −10°C 1 h and at 0°C 3 h, poured into one litre of icy water, the organic layer was separated, shaken with dilute hydrochloric acid, water, solution of sodium thiosulphate and water again. Drying

with magnesium sulphate and evaporation of the solvent yielded 17 g of raw product. The yield of azo ester obtained by twofold crystallization from ethanol (maximum temperature 40°C) was 8·5 g (31%), m.p. 73—74°C, λ_{max} 374 nm, $\varepsilon = 21$, ^{1}H-NMR (tetrachloromethane and hexadeuterodimethylsulphoxide): δ 1·07 (s, 18 H, $C(CH_3)_3$); 1·21 (s, 6 H, CH_3CO); 3·61 (s, 6 H, $COOCH_3$). For $C_{16}H_{30}N_2O_4$ (314·4) calculated: 61·12% C, 9·62% H, 8·91% N; found: 61·25% C, 9·84% H, 9·17% N.

2-Amino-2,4,4-trimethylvaleronitrile (*XII*) was prepared similarly to *IX* from 80 g 4,4-dimethyl-2-pentanone[5]. The product was extracted into ether from the reaction mixture, dried with magnesium sulphate, the solvent was evaporated, and the product was redistilled at reduced pressure. The yield was 52 g (59%) of liquid, b.p. 70—75°C/533 Pa.

Methyl ester of 2-*amino*-2,4,4-*trimethylvaleric acid* (XIII). 52 g (0·41 mol) *XII* was hydrolyzed by boiling with 300 ml hydrochloric acid for 5 h. The solution was evaporated at reduced pressure. The residue was extracted with hot methanol. The methanolic solution of 2-amino-2,44-trimethylvaleric acid thus obtained was esterified similarly to *XI*. Distillation of the raw product gave 18 g (25%) of the ester, b.p. 66°C/0·8 kPa. For $C_9H_{19}NO_2$ (173·3) calculated; 62·40% C, 11·05% H, 8·07% N; found: 62·11% C, 11·20% H, 7·62% N.

2,2-Azo-bis(methyl 2,4,4-trimethylvalerate) (*III*) was prepared from 17 g (0·098 mol) *XIII* similarly to *II*. The product was isolated at a temperature near 0°C as yellow oil, which was dissolved in petroleum ether at 0°C. On supercooling, the solution yielded a white crystalline compound, m.p. 47—49°C. Yield 4·7 g (28%), λ_{max} 372 nm, $\varepsilon = 19·7$. For $C_{18}H_{34}N_2O_4$(342·5) calculated: 63·13% C, 10·01% H, 8·18% N; found: 63·20% C, 10·09% H, 8·03% N.

2-Amino-2,4-dimethyl-4-phenylvaleronitrile hydrochloride (*XIV*) was prepared from 44 g (0·25 mol) 4-methyl-4-phenyl-2-pentanone[6] similarly to *IX*. After standing for two days, the reaction mixture was extracted with hexane, the hexane solution was evaporated at reduced pressure, and the residue was dissolved in ethanol. The ethanolic solution was filtered with active carbon, and a solution of hydrogen chloride in ether was added dropwise to the filtrate. The product was filtered by suction, washed with ether and dried *in vacuo*. The yield was 24 g (40%) of compound which did not melt up to 350°C (in a sealed capillary). For analytical purposes the hydrochloride sample was alkalized with a solution of sodium carbonate, the base was extracted into ether. From this solution hydrochloride was precipitated by adding ether saturated with hydrogen chloride. For $C_{13}H_{19}ClN_2$ (238·8) calculated: 65·39% C, 8·02% H, 11·73% N; found: 65·33% C, 8·10% H, 11·85% N.

2-*Amino*-2,4-*dimethyl*-4-*phenylvaleric acid* (XV). A suspension of 138 g (0·58) hydrochloride *XIV* in 600 ml conc. hydrochloric acid was heated 9 h with stirring on an aqueous bath, boiled 24 h under reflux, and evaporated. The crushed residue was washed with ether and extracted with methanol. The methanolic solution was evaporated, the evaporation residue was boiled with 50 ml 40% sulphuric acid 30 min. On cooling, the solution was diluted with 200 ml water and pH was adjusted to 6·5 with aqueous ammonia. The precipitate was filtered by suction, stirred in 0·5 l water, and 60 g barium carbonate powder was added. The mixture was heated with stirring 2 h on an aqueous bath. On cooling, the precipitate was filtered off and washed with hot ethanol. The aqueous and ethanolic solutions were combined and evaporated. The raw amino acid was recrystallized from 50% ethanol. Yield: 40 g (31%), m.p. 280—282°C. For $C_{13}H_{19}$. $.NO_2$ (221·3) calculated: 70·56% C, 8·65% H, 6·33% N; found: 70·32% C, 8·78% H, 6·29% N.

Methyl ester of 2-amino-2,4-dimethyl-4-phenylvaleric acid (*XVI*) was prepared from 37 g (0·167 mol) *XV* by a procedure described for *XI*. Yield 27·3 g (69·5%), b.p. 122—124°C/266 Pa. ^{1}H-NMR (tetrachloromethane and hexadeuterodimethyl sulphoxide): δ 1·10 (s, 3 H, CH_3COO); 1·33 (s, 6 H, $PhC(CH_3)_2$); 2·12 (q, 2 H, $J = 14·2$ Hz, CH_2); 3·39 (s, 3 H, $COOCH_3$); 7·04—7·36

(m, 5 H, aromate). For $C_{14}H_{21}NO_2$ (235·3) calculated: 71·46% C, 8·99% H, 5·95% N; found: 71·55% C, 9·08% H, 5·91% N.

2,2'-Azo-bis(methyl 2,4-dimethyl-4-phenylvalerate) (*IV*) was prepared from 12 g (0·05 mol) *XVI* by a procedure described for *II*. The highest temperature of the mixture in all operations was +5°C. The raw product was repurified by low-temperature crystallization from the ether–methanol mixture (3 : 1). A slightly rose-coloured compound was dissolved in the mixture ether–hexane (1·5 : 1); the solution was strongly supercooled, and a white product was obtained. Yield: 3·2 g (27%), m.p. 74—75°C, λ_{max} 371 nm, $\varepsilon = 25{\cdot}2$ ^{1}H-NMR (tetrachloromethane and hexadeuterodimethyl sulphoxide): δ 0·91 (s, 6 H, CH_3CCO); 1·36 (s, 12 H, $C_6H_5C(CH_3)_2$); 2·51 (q, 4 H, $J = 14{\cdot}2$ Hz, CH_2); 3·42 (s, 6 H, OCH_3); 7·20—7·56 (m, 10 H, aromatic). For $C_{28}H_{38}N_2O_4$ (466·6) calculated: 72·07% C, 8·21% H, 6·00% N; found: 72·03% C, 8·66% H, 5·76% N.

Kinetics of the Thermal Decomposition of Azo Compounds

The thermal decomposition of azo esters dissolved in toluene in sealed ampoules was investigated spectrometrically, by a procedure described earlier[7]. The decrease in the absorption of the azo group with time was measured with a Cary 14 spectrometer. The dependence of the logarithm D_0/D on time was linear in all cases. The decomposition proceeded as a first-order reaction. The values of the activation energy and of the pre-exponential factor were determined by the least squares method.

RESULTS AND DISCUSSION

The results of papers dealing with steric effects on the stability of tertiary azo alkanes[1,8] confirm that the largest effect on their thermal decomposition should be assigned to the branching on the γ-carbon atom with respect to the azo group, the size of substituents at the γ- or at the γ- and at the α-carbon atom also playing an important role. The decomposition of branched tertiary azo esters can be used for studying the

TABLE I

Rate Constants of Thermal Decomposition of Azo Esters *I*—*IV* and Azoalkanes[1] $R(CH_3)_2CN{=}{=}NC(CH_3)_2R$ *V*—*VIII* in Toluene Recalculated to 100°C

Compound	$k \cdot 10^5$ s^{-1}	k_{rel}	Compound[a]	$k \cdot 10^5$ s^{-1}	k_{rel}
I	124	$4{\cdot}6 \cdot 10^5$	*V*	0·00027	1
II	8	$3{\cdot}0 \cdot 10^4$	*VI*	0·0034	$1{\cdot}2 \cdot 10$
III	32 000	$1{\cdot}2 \cdot 10^7$	*VII*	0·53	$1{\cdot}9 \cdot 10^3$
IV	43 800	$1{\cdot}6 \cdot 10^7$	*VIII*	0·68	$2{\cdot}5 \cdot 10^5$

[a] *V*, R = CH_3; *VI*, R = $CH_3C(CH_3)_2$; *VII*, R = $CH_3C(CH_3)_2CH_2$; *VIII*, R = $C_6H_5C(CH_3)_2 \cdot CH_2$.

way in which the joint influence of steric and resonance effects becomes operative. The presence of the methoxycarbonyl group on the α-carbon atom greatly affects the stability of the azo compounds, its resonance energy[9] is comparatively high, contributes considerably to the decrease in the dissociation energy of the C—N bonds and leads to a lower activation energy and to an increase in the rate of decomposition. The magnitude of contribution of the resonance of the methoxycarbonyl group can be seen from a comparison between kinetic values of the thermal decomposition of similarly branched azoalkanes[1]. The decomposition temperature of azo esters is shifted to a region lower by 100°C, the activation energy decreases by 41 kJ on the average, the rate of decomposition rises by some four to five orders of magnitude, in the case of *II* by three orders of magnitude (Table I). The lower activation entropy is probably a result of the resonance stabilization, which leads to a larger planarity and restricts the freedom of conformation in the transition state.

In the series of azo esters itself considerable differences in the rate of decomposition can be seen (Table II). With increasing steric requirements the decomposition rate also increases, the difference between the relatively highest and lowest rate amounts to three to four orders of magnitude, and the activation energy decreases (Table III). A different behaviour is exhibited by *II*, the relative rate of which is about twenty times lower and the activation energy higher than those of *I*. It can be seen by using Courtauld's models that there is no important steric effect in the case of *I*, while in the case of *II* a strong agglomeration of the methyl groups may cause B-strain, in accordance with the absorption maxima[10] of the compounds: *I*, λ_{max} = = 363 nm, *II* λ_{max} = 374 nm. The steric conditions would rather favour an opposite order of the decomposition rates of both azo esters, in agreement with the results of decomposition of azoalkanes possessing a similar structure[1]. Here, an important role is played by the presence of the methoxycarbonyl group. Owing to resonance the bonds present in the methoxycarbonyl group assume the character of a double

TABLE II

Rate Constants $k_d \cdot 10^5 \cdot s^{-1}$ of the Decomposition of Azo Esters in Toluene at Various Temperatures (°C)

Compound	20	30	40	50	60	70	80	90	100	110	120	130
I	—	—	—	—	—	3·2	12·3	36·3	108	—	—	—
II	—	—	—	—	—	—	—	—	8·2	25·6	75·4	228
III	—	11·4	44·8	148	514	—	—	—	—	—	—	—
IV	3·4	13·7	54·2	195	—	—	—	—	—	—	—	—

bond, free rotation is restricted, the ester group assumes a planar arrangement with the central carbon atom. The resonance largely contributes to the stabilization of the radical formed in the decomposition, which tries to assume the most advantageous arrangement. The radical due to the decomposition of *I* can more readily assume planar arrangement than in the case of *II*, where the strong agglomeration of the methyl groups immediately adjacent to the central carbon atom is probably a hindrance to the optimum arrangement in the transition state at the beginning; consequently, more energy is required by bond stretching between the carbon and the nitrogen atoms, so that B-strain could be released first and then an optimum configuration of the radical could be achieved. These assumptions are probably the cause of the different stability of the two compounds. *III* and *IV*, the chain of which is branched at the γ-carbon atom, decompose faster than *II* by four orders of magnitude. This branching, as illustrated by the models, gives rise to a strong F-strain, which together with B-strain may cause bond stretching between the carbon and the nitrogen atoms in the transition state, thus creating better conditions for an optimum arrangement of the forming radical without such high energy requirements as those of *II*, in agreement with the lower activation energy values of these compounds (Table III).

III was used as initiator in the polymerization of styrene in toluene at 20°C, 25° and 35°. Its efficiency is high particularly at lower temperatures, as documented by the following values: $f = 0{\cdot}918$ (20°C), 0·767 (25°), 0·531 (35°C) (ref.[11]).

The results show that cooperation of intensive steric effects due particularly to the branching at the γ-carbon atom and of substituents at the α-carbon atom able to stabilize the radical by resonance allows to obtain the maximum acceleration of the decomposition of tertiary azo compounds, which may become operative as initiators of radical polymerization at relatively low temperatures.

TABLE III
Kinetic Quantities of Thermal Decomposition of Azo Esters in Toluene

Compounds	E_a kJ/mol	log *A*	$H^{\neq}$ kJ/mol	$G^{\neq}$ kJ/mol	$S^{\neq}$ kJ/mol K	k_{rel} at 60°C
I	127·3 ± 2·1	14·87 ± 0·33	124·3 ± 2·1	114·3 ± 4·2	30·1 ± 6·3	2·3 . 10
II	139·0 ± 1·3	15·39 ± 0·18	136·0 ± 1·3	122·7 ± 2·5	40·2 ± 3·3	1·0
III	106·3 ± 1·3	14·39 ± 0·24	103·8 ± 1·3	96·7 ± 2·9	21·3 ± 4·6	$1{\cdot}4 \cdot 10^4$
IV	106·3 ± 0·8	14·46 ± 0·16	103·4 ± 0·8	97·9 ± 2·1	22·6 ± 2·9	$1{\cdot}8 \cdot 10^4$

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