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ON THE MECHANISM OF FORMATION OF DIMERIC AND REDUCED PRODUCTS FROM AN α-HALO AMIDE WITH SODIUM METHOXIDE

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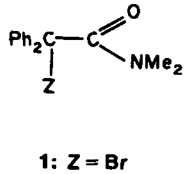
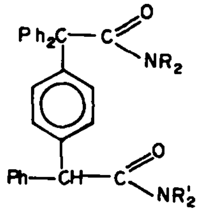
Abstract—Treatment of 2-bromo-N,N-dimethyl-2,2-diphenylacetamide 1 with sodium methoxide in 2,2-dimethoxypropane furnishes mixtures of the reduced product 2 and the dimer 5. Crossing experiments have shown that 2 is *not* a precursor of 5, supporting thereby the $S_{RN}1$ mechanism for the formation of both 5 and 2.

Recently 2-bromo-N,N-dimethyl-2,2-diphenylacetamide (1) was shown to yield with excess sodium methoxide in 2,2-dimethoxypropane (DMP) the reduced product 2 and a "dimer" of structure 5, in addition to minor amounts of the 2-hydroxy (3) and the 2-methoxy analogues (4) of the starting compound. The formation of compound 5 was considered as an indication of the presence of radicals 10 in the reaction mixture, the radicals themselves being probably formed through the intermediacy of the radical-anions 9.[1] Thus, the formation of both compounds 2 and 5 appeared to involve the $S_{RN}1$ mechanism,[2–5] see Chart 1. (For the formation of dimeric by-products in $S_{RN}1$ reactions, see, e.g. Refs 6, 7.)



1: Z = Br
2: Z = H
3: Z = OH
4: Z = OMe



5: R = R′ = Me
6: R_2 = $-(CH_2)_4-$, R′ = Me
7: R = Me, R'_2 = $-(CH_2)_4-$
8: R_2 = R'_2 = $-(CH_2)_4-$

In order to support the mechanisms depicted in Chart 1, two alternative pathways of formation of compound 5 had to be ruled out. Both additional pathways would involve the intermediacy of compound 2 which, after deprotonation to 11 by excess methoxide, would yield, with unchanged 1, compound 5 by rearrangement of intermediately formed 12 and/or 13 (Chart 2). (For the related rearrangement of tetraphenylsuccinonitrile, see Ref. 9.) If mechanisms a and/or b of Chart 2 contributed to the formation of compound 5, compound 6 and compounds 6 and 7, respectively, should be formed, in addition to 5, in the reaction of compound 1 and sodium

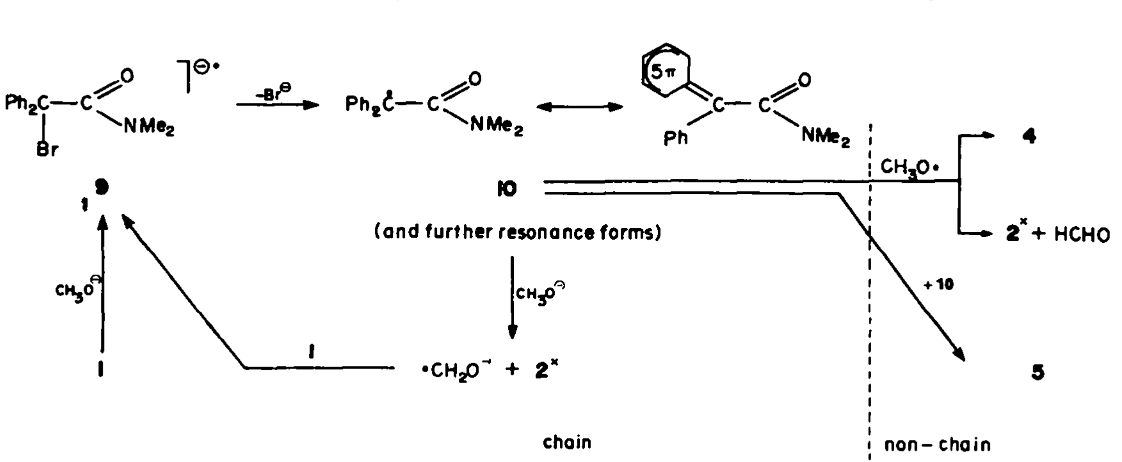


Chart 1.

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[x] Formation of compound 2 does not necessarily involve direct uptake of a hydrogen atom at the α-position of 10; it may proceed as well by attachment of hydrogen to one of the *p*-positions of 10 and subsequent rearrangement of the resulting cyclohexadiene to 2, cf. Ref. 8

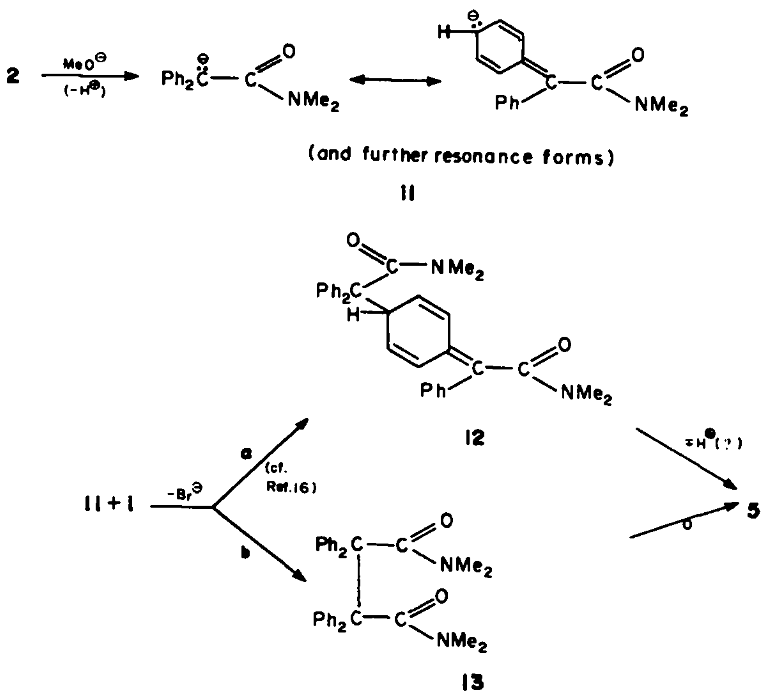
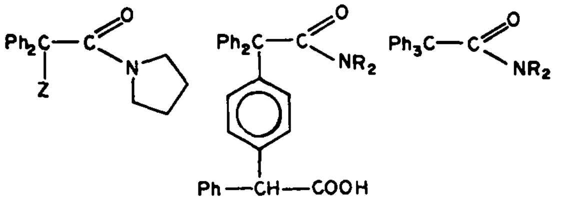


Chart 2.

methoxide carried out in the presence of the pyrrolidide **14**. Similarly, compound **7** and compound **6** and **7**, respectively, should be obtained, in addition to compound **8**, in the reaction of compound **15** with sodium methoxide carried out in the presence of compound **2**.



14: Z = H
15: Z = Br
16: Z = OH
17: Z = OMe

18: R = Me
19: $R_2 = -(CH_2)_4-$

20: R = Me
21: $R_2 = -(CH_2)_4-$

Authentic samples of the mixed dimers **6** and **7** were obtained by selective hydrolysis of the 2,2-diarylacetamide moieties of the dimers **8** and **5** (the former being obtained, similarly to the dimer **5**, by allowing compound **15** to react with sodium methoxide in DMP) to yield the monoamides **19** and **18**, respectively, which were treated with thionyl chloride and, subsequently, with dimethyl amine and pyrrolidine, respectively. In the TLC system used, the four dimers **5**–**8** had identical R_f values but were cleanly separated from compounds **2**–**4**, **14**, **16** and **17**. Accordingly, the dimer fractions of the crossing experiments were separated from the remaining products and examined by NMR. In no case were even trace amounts of the mixed dimers **6** and **7** detected.[a] The mechanisms depicted in Chart 2 are therefore ruled out[b] and the mechanisms of Chart 1 are substantiated. This appears to be the first case of formation, by the $S_{RN}1$ mechanism, of *substantial* amounts of reduced products from *aliphatic* halogen derivatives.

The results of the reactions of compounds **1** and **15** with methoxide, both in the absence and presence of added **14** and **2**, respectively, are compiled in Table 1. Part of the reactions were run under argon but the exclusion of oxygen had at least no pronounced effect on the product distribution. This, however, does not rule out neither the chain[4,11] nor the non-chain mechanism[12] of Chart 1. The relative amounts of the compounds **3** and **4** in the reaction products obtained from compound **1** decreased sharply with increasing reaction time. This suggests that a substantial part of these compounds is formed via hydrolysis and methanolysis, respectively, of unchanged starting compound during work-up, i.e. that reaction **10** + MeO· → **4** is not an efficient one.

^{1}H NMR *spectra of the dimers* 5–8

The signals of one N-Me group in the ^{1}H NMR spectrum of the dimer **5**, as well as of two α-protons of the pyrrolidine groups in the spectrum of the dimer **8** are considerably shifted upfield (by about 0.6 and 1.0 ppm, respectively) as compared with the positions of the signals of the remaining three N-Me groups and the remaining six α-protons, respectively. Comparison of the ^{1}H NMR spectrum of the dimer **5** with those of the 2,2-diaryl-N,N-dimethylacetamides **2** and **6** and the 2,2-triaryl-N,N-dimethylacetamides **7**, **18** and **20** reveals that the high-field signal arises from one of the N-Me groups

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[a] The sensitivity of the method is demonstrated by the ready detection of 0.54 mole% of **8** admixed to the dimer **5**.

[b] Indeed, on the basis of the results of the crossing experiments any other mechanism of formation of the dimeric products **5** and **8** which would require the intermediacy of the reduced products **2** and **14** and/or of their anions (e.g. **11**), including that which could be formulated to the analogy of the mechanism of the base-induced dimerization of 2-nitropropane and of *p*-nitrotoluene,[10] are also ruled out.

Table 1. Reaction of the 2-bromo-2,2-diphenylacetamides 1 and 15 with NaOMe in 2,2-dimethoxypropane (DMP) at room temperature^a

Starting compound			NaOMe		DMP	Added reagent			Time	Products^b and yields(%)			
	g	mmoles	g	mmoles	ml		g	mmoles	hr	2^c or 14^d	3^c or 16^d	4^c or 17^d	5^c or 8^d
1^e	4.0	12.5	3.6	67.0	40	—			2	20	9	12	24
1^f	5.5	17.3	2.1	38.9	30	—			4	15	21	15	16
1	1.0	3.14	0.88	16.3	10	—			4	28	9	—	23
1	1.0	3.14	0.88	16.3	10	—			4	27	16	—	20
1	1.0	3.14	0.68	12.6	10	—			24	40	—	—	30
1	2.0	6.28	2.7	50.2	40	14	1.67	6.28	120	^{g}	^{g}	^{g}	28^h
15	4.0	11.6	2.5	46.0	40	—			48	35	7	4	32
15	2.0	5.8	3.0	55.5	40	2	1.39	5.8	24	^{g}	^{g}	^{g}	27^h

[a] For details, see Experimental

[b] All products, except compounds 5 and 8 were identified by comparison with authentic samples. The assignments of structure to compounds 5 and 8 are based on their IR, NMR and mass spectra.

[c] From compound 1

[d] From compound 15

[e] Under Ar

[f] Under N_2

[g] No attempt was made to isolate these products

[h] Not contaminated, according to NMR, by 6 or 7. In the TLC system used the dimers 5–8 have identical R_f values

of the 2,2,2-triaryl-N,N-dimethyl acetamide moiety of 5. $\Delta\nu_{tri}$ for the two Me signals of this moiety is about 60 Hz, while $\Delta\nu_{di}$ for the two Me signals of the 2,2-diaryl-N,N-dimethylacetamide moiety is about 3 Hz in CCl_4. From the temperature dependence of the ^1H NMR spectrum the following values were calculated[13] for the barriers of rotation of the two N-Me_2 groups of compound 5: $\Delta G^{\neq}_{tri} = 15.3$ kcal/mole at $T_{c,tri} = 40°$, and $\Delta G^{\ddagger}_{di} \approx 17.2$ kcal/mole at $T_{c,di} \approx 40°$; as a result of the small $\Delta\nu_{di}$, the latter values have to be regarded as approximate. The $\Delta G^{\ddagger}_{tri} < G^{\ddagger}_{di}$ relation may be explained by noting that even the most stable conformation of the 2,2,2-triaryl-N,N-dimethylacetamide moiety is strained.

Similarly, from a comparison of the ^1H NMR spectra of the dimer 8, the N-(2,2-diarylacetyl)pyrrolidines 7 and 14, and the N-(2,2,2-triarylacetyl)pyrrolidines 6, 19 and 21 it follows that the high-field α-proton signal in the spectrum of 8 arises from two α-methylene protons of the pyrrolidine ring of the N-(2,2,2-triarylacetyl)pyrrolidine moiety of 8.

In the mixed dimer 6 the rotation of the pyrrolidine group is hindered ($\Delta G^{\neq} = 16.0$ kcal/mole at $T_C = 62°$ in C_2Cl_4) but the rotation of the dimethylamino group is free even at room temperature. The opposite is true for the mixed dimer 7; a value of $\Delta G^{\neq} = 15.2$ kcal/mole at $T_c = 39°C$ (which are in agreement with the $\Delta G^{\ddagger}_{tri}$ and $T_{c,tri}$ values found for compound 5) was found for the rotation of the dimethylamino group of the dimer 7 in C_2Cl_4.

The aromatic region of the spectra of all four dimers exhibit three sharp singlets within an interval of 0.25–0.30 ppm. This (as well as the presence of a band at 800 cm^{-1} in the IR spectra of the dimers) is taken as evidence for the presence of a *p*-phenylene group in the dimers; in the presence of *o*-phenylene groups the aromatic region should, presumably, be of a completely different pattern.

EXPERIMENTAL

Syntheses of the 2-bromo-2,2-diphenylacetamides 1 and 15

(a) A mixture of 2,2-diphenylacetyl chloride (46 g; 0.2 moles) and Br_2 (11 ml; 0.2 moles) was stirred at 80–100° until the colour of the Br_2 disappeared (about 1 hr). An additional amount (2 ml) of Br_2 was added and stirring was continued for another 0.5 hr. The mixture was cooled to 0° and triturated with light petroleum to obtain 2-bromo-2,2-diphenylacetyl chloride. The crystalline product was dissolved in $CHCl_3$ (100 ml), and an ethereal soln of dimethylamine was added by drops with stirring at 0° until the mixture became permanently alkaline. The soln was washed with water, dried ($MgSO_4$) and concentrated to about 100 ml. On cooling, 25 g (40%) of cd 1, m.p. 129° (from gasoline). [Found: C, 60,64; H, 5.35; N, 4.28. Calc. for $C_{16}H_{16}BrNO$ (318.22): C, 60.39; H, 5.07; N, 4.40%], separated. IR (KBr): 1640 cm^{-1}.

(b) Crude 2-bromo-2,2-diphenylacetyl chloride (20.9 g; 66.5 mmoles), obtained from 2,2-diphenylacetyl chloride (20 g; 86.7 mmoles) and Br_2 as described, was dissolved in $CHCl_3$ (100 ml) and treated under stirring and ice-water cooling with a soln of pyrrolidine (9.5 g: 133 mmoles) in $CHCl_3$ (20 ml). The mixture was stirred for another hr, washed with water, dried ($MgSO_4$) and evaporated to dryness. The oily product was crystallized from gasoline to obtain 9.3 g (31%) of 15, m.p.: 114–115° (Found: Br, 23.51; N, 4.35. Calc. for $C_{18}H_{18}BrNO$ (344.24): Br, 23.21; N, 4.07%); IR (KBr): 1650 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 1.75, bs, 4H β-CH_2 groups; 3.2 and 3.65, bs's, 2H, each, α-CH_2 groups; 7.3 ppm, s, 10H.

(c) An ethereal soln of N-bromodimethylamine was added with stirring and ice-salt cooling to the solon of diphenyl ketene (5.5 g; 27.8 mmoles) in anhyd ether (50 ml) until the bromoamine was in excess (positive reaction with KI). The mixture was stirred for another 0.5 hr to obtain a crystalline product which was recrystallized from gasoline. 3.6 g (41%) of compound 1, m.p.: 129°, identical with the product obtained according to (a), resulted.

N,N-*Dimethyl-2,2-diphenylacetamide* (2)[14]. Authentic product: IR (KBr): 1625 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.0, s, 6H; 5.2. s. 1H; 7.25 ppm, s, 10H.

2,2-*Diphenylacetyl pyrrolidide* (14). Pyrrolidine (4.7 g; 66.2 mmoles) was added by drops with stirring and ice-water cooling to a soln of 2,2-diphenylacetyl chloride (5.9 g; 25.6 mmoles) in $CHCl_3$ (20 ml). The mixture was washed with water, N HCl and water, dried ($MgSO_4$) and evaporated to dryness. The crystalline residue was recrystallized from EtOH to yield 3.9 g (57%) of 14, m.p.: 164–165°. (Found: C, 81.22; H, 7.33; N, 5.20. Calc. for $C_{18}H_{19}NO$ (265.34): C, 81.47; H, 7.22; N, 5.28%); IR (KBr): 1620 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.85, bs, 4H; 3.3–3.7, m, 4H; 5.05, s, 1H; 7.25 ppm, s, 10H.

Synthesis of the 2-methoxy-2,2-diphenylacetamides 4 and 17

(a) Compound 1 (0.5 g; 1.6 mmoles) was refluxed for 1/2 hr with anhyd MeOH (5 ml) to yield, after cooling, 0.32 g (76%) of 4, m.p.: 127° from gasoline. (Found: C, 75.62; H, 7.15; N, 5.48. Calc. for $C_{17}H_{19}NO_2$(269.33): C, 75.81; H, 7.11; N, 5.20%); IR (KBr): 1640 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.9, bs, 6H; 3.3, s, 3H; 7.1–7.5 ppm, m, 10H.

(b) Compound 15 (1.0 g; 2.9 mmoles) was refluxed with anhyd MeOH (10 ml) for 4 hr. The mixture was evaporated to dryness and the oily residue crystallized from gasoline to yield 0.38 g (44%) of 17, m.p.: 99–100°. (Found: C, 77.20; H, 7.05; N, 4.58. Calc. for $C_{19}H_{21}NO_2$ (295.37): C, 77.26; H, 7.17; N, 4.74%); IR (KBr): 1645 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.55–2.0, m, 4H; 3.25, s, 3H; 3.1–3.4, m, 2H; 3.4–3.75, m, 2H; 7.1–7.65 ppm, m, 10H.

2-Hydroxy-2,2-diphenylacetyl pyrrolidide (16). Water (30 ml) was added by drops to a stirred solon of 15 (0.76 g; 2.2 mmoles) in DMSO (10 ml) to obtain 0.49 g (79%) of 16, m.p.: 106–107°, lit.[15] m.p.: 106°. (Found: C, 76.73; H, 6.70; N, 4.72. Calc. for $C_{18}H_{19}NO_2$ (281.34): C, 76.84; H, 6.81; N, 4.98%); IR (KBr): 3350, 1610 cm^{-1}.

Reaction of the 2-bromo-2-diphenylacetamides 1 *and* 15 *with* NaOMe *in 2,2-dimethoxypropane* (Table 1)

(a) Mixtures of 1, NaOMe and DMP were stirred at room temp. for 2–24 hr, subsequently acidified with HClaq and extracted with ether. The ethereal solns were dried ($MgSO_4$) and evaporated to dryness. The oily residues were worked up by column chromatography (Kieselgel 60, Merck, Korngrösse 0.063-0.200 mm; solvent: benzene with gradually increasing amounts of added acetone, to end up with benzene-acetone, 1:1, v/v), and the individual fractions obtained were purified by TLC (Kieselgel $PF_{254+366}$, Merck; solvent as above) to obtain the following products in the yields shown in Table 1.

Compound 2, m.p.: 135–136°, lit.[14] m.p.: 130°, identical (IR, NMR) with an authentic sample (see above). Compound 3, m.p. and lit. m.p.: 131–132°, identical with an authentic sample.[16] Compound 4, m.p.: 127° (gasoline), identical with an authentic sample (see above). Compound 5, m.p.: 160–161° (acetone-light petroleum);[c] (Found: C, 80.21; H, 6.78; N, 6.13. Calc. for $C_{32}H_{32}N_2O_2$ (476.60): C, 80.64; H, 6.77; N, 5.88%); IR (KBr): 1650, 800 cm^{-1}, w, ^{1}H NMR (CCl_4): δ 2.34, bs, 3H; 2.94, s, and 2.97, s, total 9H;[d] 5.07, s, 1H; 6.98, 7.06 and 7.14 ppm, all s's, total intensity 19H; MS (150°C): *m/z* 476 (3.4%, $C_{32}H_{32}N_2O_2$, M^+); 405 (25%); 404 (73%, M $\overset{*}{-}$ $CONMe_2$); 360 (0.54%); 359 (1.7%, 404 $\overset{*}{-}$ Me_2NH); 333 (5.4%); 332 (15%, 404 $\overset{*}{-}$ $CONMe_2$); 253 (4.2%, Ph_3C_2-2H); 252 (3.1%, Ph_3C_2-3H); 241 (5.4%, Ph_3C-2H): 239 (3.1%); 222 (3.5%); 165 (5.8%, $C_{13}H_9^+$); 72 (100%, 404 $\overset{*}{-}$ 332).

(b) The reaction of 15 and NaOMe in DMP was carried out similarly and gave the following products in the yields shown in Table 1: compound 16, m.p.: 106–107°, 17, m.p.: 99–100°, and 14, m.p.: 164–165°, all identical with the respective authentic samples (see above). Compound 8, m.p.: 90–110° (amorphous product, from aqueous MeOH) (Found: N, 5.41; calcd. for $C_{36}H_{36}N_2O_2$ (528.67): N, 5.30%); IR (KBr): 1620, 800 cm^{-1}, w; ^{1}H NMR (CCl_4): δ 1.5–2.0, m, 8H, β-CH_2 groups of the pyrrolidine rings; 2.42, distorted t, 2H, and 3.35–3.7, m, 6H, α-CH_2 groups of the pyrrolidine rings;[e] 4.93, s, 1H; 7.05, 7.12 and 7.25 ppm, all s's, total intensity 19H; MS (220°C): *m/z* 528.2894 (5%, $C_{36}H_{36}N_2O_2$, $M^{+\cdot}$); 430, (80% M $\overset{*}{-}$ $CONC_4H_8$); 415 (1%); 332 (8%, M − 2 $CONC_4H_8$); 264 (0.6%, M^{2+}); 253 (2%, Ph_3C_2-2H); 252 (2%, Ph_3C_2-3H); 241 (2%, Ph_3C-2H); 165 (3%, $C_{13}H_9^+$); 98 (100%, $CO\overset{+}{N}C_4H_8$); 70 (3%, 98 − 28); 55 (50%).

(c) The crossing experiments and the work-ups of the resulting mixtures were carried out similarly, except that (1) mixtures of compounds 1 and 14, and 15 and 2, respectively, were treated with NaOMe in DMP, and that (2) only the dimeric fractions (5 and 8, respectively) were isolated. For details, see Table 1.

Synthesis of the mixed dimers 6 and 7

(a) A mixture of the dimer 8 (0.42 g; 0.8 mmoles), conc H_2SO_4, AcOH and H_2O (5 ml, each) was refluxed for 15 hr and poured into H_2O (40 ml). The crystalline product was worked up by tlc (Kieselgel $PF_{254+366}$; benzene-acetone, 2:1) to yield 0.08 g (19%) of unchanged 8 and 0.21 g (55%) of the monoamide 19 as an amorphous product (from aqueous AcOH) which turned crystalline at 100–110° in the m.p. capillary and melted at 233–234°. (Found: N, 3.07. Calc. for $C_{32}H_{29}NO_3$ (475.56): N, 2.95%); IR (KBr): 3300–2700, 1715 with sh at 1705, 1595 with sh at 1620, 800 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.65, bs, 4H, β-CH_2 groups of the pyrrolidine ring: 2.45, distorted *t*, and 3.45-3.90, M, 2H, each, α-CH_2 groups of the pyrrolidine ring; 4.9, bs, 1H; 7.0–7.4 ppm, m, 19H. MS (180°C): *m/z* 475.2139 ($C_{32}H_{29}NO_3$), 4% $M^{+\cdot}$); 430 (1%, M-COOH); 377 (100%, M − $CONC_4H_8$); 360 (0.5%); 359 (0.5%); 338 (0.2%); 333 (12%, 377 − CO_2); 332 (30%, 377 − COOH); 248 (0.5%); 243 (0.3%); 98 (12%, $CO\overset{+}{N}C_4H_8$).

(b) The monoamide 19 (0.31 g; 0.65 mmoles) was refluxed with $SOCl_2$ (5 ml) for 1 hr. The excess reagent was distilled off and the residue stirred for 2 hr at room temp. with excess dimethylamine in ether. The mixture was washed with water (10 ml), the aqueous layer with ether (two portions, 10 ml, each). The combined etheral solns were washed with dil. HClaq (two portions, 10 ml, each) and water (10 ml), dried ($MgSO_4$) and evaporated to dryness. The residue was worked up by tlc (Kieselgel $PF_{254+366}$; benzene-acetone, 7:3) to obtain 0.18 g (55%) of the mixed dimer 6 as an amorphous product, m.p.: 80–100° from aqueous EtOH. (Found: C, 80.70; H, 6.88; N, 5.52. Calc. for $C_{34}H_{34}N_2O_2$ (502.66): C, 81.24; H, 6.82; N, 5.57%); IR (KBr): 1630, 805 cm^{-1}, w. ^{1}H NMR ($CDCl_3$): δ 1.5–2.0, m, 4H, β-CH_2 groups of the pyrrolidine ring; 2.47, t, and 3.65, t, 2H, each, α-CH_2 groups of the pyrrolidine ring; 3.05, s, 6H; 5.21, s, 1H; 7.1, 7.2 and 7.25 ppm, all s's total intensity 19H. ^{1}H NMR (C_2Cl_4); δ 1.25–1.75, m, 4H, β-CH_2 groups; 2.40 and 3.55, distorted t's, 2H, each, α-CH_2 groups of the pyrrolidine ring; 2.87, s, 6H; 5.10, s, 1H; 7.0–7.4 ppm, m, 19H. MS (180°C): *m/z* 475.2139 ($C_{32}H_{29}NO_3$, 7%, $M^{+\cdot}$); 446 (1%, M − C_4H_8); 430 (1%, M − $CONMe_2$); 420 (0.5%); 404 (100%, M $\overset{*}{-}$ $CONC_4H_8$); 387 (1%); 359 (0.3%, 404 $\overset{*}{-}$ 45): 347 (0.5%); 340 (0.2%); 333 (1%); 332 (2%, 404 $\overset{*}{-}$ $CONMe_2$); 248 (1%); 98 (4%, $CO\overset{+}{N}C_4H_8$); 72 ($CO\overset{+}{N}Me_2$).

(c) A mixture of the dimer 5 (0.86 g; 1.8 mmoles), conc H_2SO_4, AcOH and water (5 ml, each) was refluxed for 8 hr and poured into water (50 ml). The crystalline product was dissolved in N NaOH, reprecipitated with dil HCl and recrystallized from benzene to yield 0.46 g (57%) of 18, m.p.: 212–213°. (Found: C, 80.31; H, 6.01; N, 3.34. Calc. for $C_{30}H_{27}NO_3$ (449.53): C, 80.15; H, 6.06; N, 3.12%); IR (KBr): 3300–2900, 1740, 1605 with sh at 1650, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.35 and 3.0, bs's, 3H, each; 4.9, s, 1H; 7.12, 7.20 and 7.28 ppm all s's, total intensity 19H. MS (180°): *m/z* 449.2001 ($C_{30}H_{27}NO_3$), 10%, $M^{+\cdot}$); 405 (0.5%); 404 (1.5%, M − COOH); 377 (100%, M $\overset{*}{-}$ $CONMe_2$); 333 (4%, 405 − $CONMe_2$); 332 (4%, 377 − COOH); 243 (0.4%); 222 (1%); 72 (4%, $CO\overset{+}{N}Me_2$).

(d) The monoamide 18 (0.46 g; 1 mmole) was refluxed with $SOCl_2$ (5 ml) for 1 hr and the excess reagent was distilled off *in vacuo*. The oily residue was dissolved in dry ether (10 ml), pyrrolidine (0.5 ml) was added, and the mixture stirred for 2 hr. Work-up of the mixture was performed as described under (c). 0.34 g (66%) of the dimer 7 was obtained as an amorphous product, m.p.: 80–100° from aqueous EtOH. (Found: N, 5.23. Calc. for $C_{34}H_{34}N_2O_2$ (502.66): N, 5.57%); IR (KBr): 1630 vs, 800 cm^{-1} w. ^{1}H NMR ($CDCl_3$): δ 1.8–2.0, m, 4H, β-H's of pyrrolidine ring; 2.37, s, 3H; 3.06, s 3H; 3.40–3.65, m, 4H, α-H's of pyrrolidine ring; 5.07, s, 1H; 7.1–7.35 ppm, m, 19H. ^{1}H NMR (C_2Cl_4): δ 1.64–1.82, m, 4H; 2.26, bs, 3H; 2.89, bs, 3H; 3.27–3.5, m, 4H; 4.95, s, 1H; 6.9–7.3 ppm, m, 19H. MS (180°C): *m/z* 502.2622 ($C_{34}H_{34}N_2O_2$, 10%, $M^{+\cdot}$); 446 (0.2%, M − C_4H_8); 430 (100%, M $\overset{*}{-}$ $CONMe_2$); 420 (0.5%); 413 (0.2%); 404 (2%, M − $CONC_4H_8$); 359 (0.2%); 347 (0.1%); 333 (0.5%); 332 (1%, 430 − $CONC_4H_8$); 222 (1.5%); 155 (1.5%); 129 (1.5%); 98 (10%, $CO\overset{+}{N}C_4H_8$); 92 (10%); 72 (1%, $CO\overset{+}{N}Me_2$).

N,N-*Disubstituted 2,2,2-triphenylacetamides*

(a) A soln of dimethylamine in ether was added by drops with stirring to a soln of triphenylacetyl chloride[17] (0.7 g; 2.3 mmoles)

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[c] Compound 5 crystallizes extremely sluggishly. From aqu. MeOH it is obtained as an amorphous material, melting between 8–100°C

[d] For a discussion of the N-Me region of the spectrum, see above

[e] For a discussion of the pyrrolidine signal region of the spectrum, see above

in $CHCl_3$ (5 ml) at room temp. until the mixture became permanently alkaline. The mixture was evaporated to dryness on the next morning and the residue triturated with water to yield 0.6 g (83%) of crystalline **20**, m.p.: 216–217°, lit.[18] m.p.: 217.5° (Found: C, 83.66; H, 6.75; N, 4.36. Calc. for $C_{22}H_{21}NO$ (315.40): C, 83.77; H, 6.71; N, 4.44%); IR (KBr): 1640 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.35 and 3.05, bs's, 3H, each; 7.25 ppm, s, 15H.

(b) A mixture of triphenylacetyl chloride (0.62 g; 2 mmoles), pyrrolidine (0.5 ml) and dry benzene (3 ml) was refluxed for 3 hr and evaporated to dryness. The residue was triturated with water to yield 0.62 g (90%) of **21**, m.p.: 187° from EtOH. (Found: C, 84.43; H, 6.79; N, 3.80. Calc. for $C_{24}H_{23}NO$ (341.43): C, 84.42; H, 6.78; N, 4.10%); IR (KBr): 1630 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.7, bs, 4H, β-CH_2 groups; 2.3–2.65, m, and 3.65, distorted *t*, 2*H*, each, α-CH_2 groups: 7.2 ppm, s, 15H.

IR spectra were run on a Spektromom 2000 spectrometer (Hungarian Optical Works, Budapest) mass spectra were obtained at 70 eV with an AEI MS-902, equipped with a direct inlet system. The ^1H NMR spectra of the dimeric compounds **5–8** were recorded at 100 MHz with a JEOL PS-100, those of the other compounds at 60 MHz with a Perkin-Elmer R-12 spectrometer, using TMS as internal reference in both cases.

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