Single-electron Transfer-initiated Thermal Reactions of Arylmethyl Halides. Part 8.[1] The Reaction of 2-Halogeno-*NN*-dimethyl-2,2-diphenylacetamides with Sodium Methoxide in 2,2-Dimethoxypropane. The Effects of Added Acetone, Temperature Elevation, and of the Nature of the Halogen. Refinement of the Reaction Mechanism

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In addition to the previously isolated products (**1c**) and (**2a**), trimeric (**2b**) and oligomeric products (**2c**) were shown to result from the title reaction. The reactions leading to all these products are initiated by single-electron transfer (SET) to the halogenoacetamides (**1a** and **b**). The operation of chain processes is established (Scheme 4). Acetone enolate is shown to be a more effective single-electron donor towards compound (**1a**) than methoxide. In the absence of acetone enolate S_N reactions with methoxide compete with SET-initiated reactions of compound (**1a**) at room temperature. Temperature elevation favours SET over S_N reactions. The mechanism of trimer (**2b**) and oligomer (**2c**) formation is discussed and, in addition to the radical recombination mechanism, the carbanionic mechanism of dimer (**2a**) formation is established. The chloro derivative (**1b**) is shown to be less reactive in the title reaction than the bromo analogue (**1a**).

Some time ago we reported on the reaction of the 2-bromo-2,2-diphenylacetamide (**1a**) with sodium methoxide in 2,2-dimethoxypropane (DMP) at ambient temperatures which furnished mainly the reduction product (**1c**) and the dimer (**2a**).[2] Formation of the latter and preliminary mechanistic studies suggested the operation of a radical anion–radical chain mechanism[2–4] [Scheme 1, equations (1)—(5)]. As an alternative to equation (3) a two-step process with the intermediacy of the anion $R_{-H}^{\cdot -}$ = (**5**), *viz.* reduction of the radicals (**3**) by electron donors present in the reaction mixture, followed by protonation [equation (6)] was also envisaged.[4b]

Recent experimental observations have shown that, while the mechanism originally suggested for the title reaction is essentially correct (in particular as regards its chain character), the reaction is more complex than originally assumed, and the mechanism has therefore to be refined. Here we discuss the refined mechanism of the title reaction, as well as the effect of the replacement of bromine in the starting compound (**1a**) by chlorine. Furthermore, exact proof for the chain nature of the title reaction will be presented.

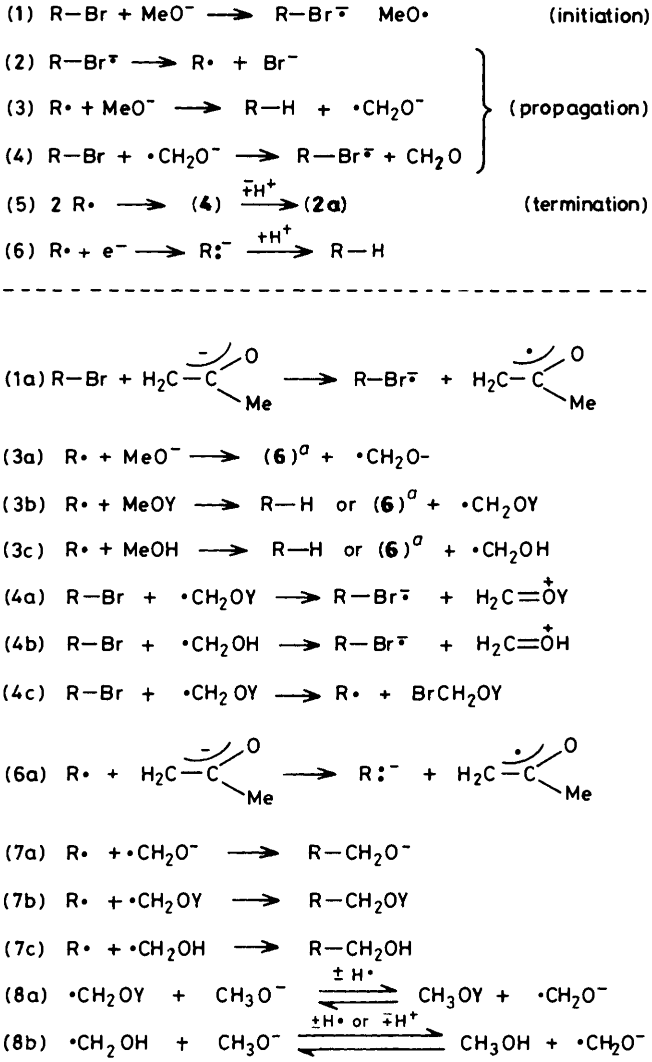
Results and Discussion

The Initiation Step. Initiation by Acetone Enolate. Product Composition as a Function of the Amount of Enolate Present.— In our previous studies[2,3] the solvent DMP had not been specially purified. When using DMP which had been refluxed with and freshly distilled from lithium aluminium hydride (LAH), we have now found that the starting bromo derivative (**1a**) reacted considerably slower and that a greater variety of products was formed (Table 1, entries 1 and 2). The formation of the *tele*-substitution products (**7**)[2,5,†] is significant. Since these products are formed from (**1a**) only in the presence of sodium methoxide,[5] their formation must take place *during the reaction* while the *ipso*-substitution product (**1d**) may be formed both during the reaction and during work-up (*cf.* ref. 5). Furthermore, since formation of the *tele*-substitution products (**7**) involves a classical S_N' process with subsequent deprotonation–protonation[5] (*cf.* Scheme 5 and ref. 6), this means that in specially purified solvent DMP nucleophilic substitution of compound (**1a**) is able to compete effectively with single electron transfer (SET) to compound (**1a**). Clearly the DMP used in our early experiments contained some contaminant which promotes SET to the bromo derivative (**1a**) and which is removed by treatment with LAH. The two most probable contaminants of DMP are, of course, methanol and acetone (both of which are removed by treatment with LAH), and the latter indeed proved to be responsible for the observed effect because addition of one or more mol. equiv. acetone to the reaction mixture (Table 1, entries 3—5) greatly enhanced the rate of formation of the SET products (**1c**) and (**2a**) and, at the same time, completely suppressed the formation of other products (compare with entry 2). This effect of acetone is readily understood since its deprotonation by methoxide furnishes the enolate which is known[7,8] to be an effective single-electron donor. This means that in the presence of acetone an additional initiation step [equation (1a)] operates by which, if the amount of added acetone is sufficiently high, the initiation step shown in equation (1) may be practically completely suppressed. Moreover, it is reasonable to assume that any other carbanionic species (see below) present in the reaction mixture may initiate the formation of SET products from compound (**1a**).

The yield of the reduction product (**1c**) steadily increases with the amount of acetone added (Table 1, entries 2—5). A similar effect of added acetone had been observed in the thermolysis of the phenylazo derivative (**1f**),[1] and is, in both cases, the result of acetone enolate being an effective single-electron donor,[7] able to reduce the radicals (**3**) to the anions (**5**) [equation (6a)].

When the amount of added acetone was reduced to 0.3 mol. equiv. (Table 1, entries 6 and 7), the reaction became

† *ortho–para* ratio (^{1}H n.m.r.) 12:88.



Scheme 1.[c] R-Br = (**1a**), R-H = (**1c**), R$^{\bullet}$ = (**3**), R$:^{-}$ = (**5**), Y = CMe_2OMe, *i.e.* MeOY = DMP

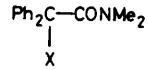
[a] The isomeric *o*-cyclohexadiene is another likely product. [b] Methanol is always present in the reaction mixture as a result of deprotonation of the cyclohexadiene (**4**), (**6**), and (**11**), and of acetone by methoxide ions (see below). [c] For the reactions below the dotted line, see later.

considerably slower, the yield of compound (**1c**) significantly decreased and, in addition to the dimer (**2a**), significant amounts of the trimer (**2b**) were isolated.

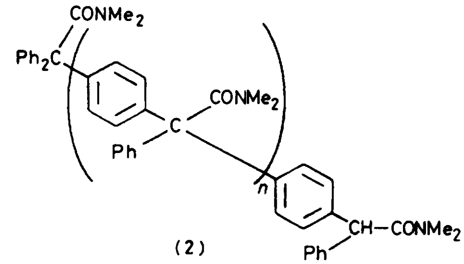
Further reduction of the amount of added acetone (Table 1, entry 8) leads to predominant formation of a mixture of oligomers (**2c**) differing in the value of *n*.

Proof of the Structures of the Trimer (**2b**) *and the Oligomers* (**2c**) *and the Mechanism of their Formation*.—The mass spectrum of the trimer exhibited diagnostic peaks at m/z 713 ($M^{+\bullet}$), 641, 569, 497 (corresponding to the loss of one, two and three $CONMe_2$ groups, respectively, of atomic mass 72), and 72. This unambiguously established the trimeric nature of the product. Its structure was established on the basis of mechanistic considerations and the ^1H and ^{13}C n.m.r. spectra.

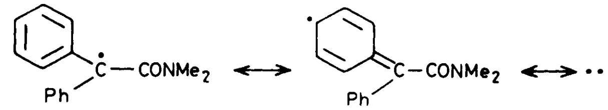
All types of S_R-Ar pathways of formation of the trimer (**2b**), *viz.* reactions of the dimer (**2a**) with radical (**3**), are ruled out because the trimer (**2b**) has never been observed[1,4,5] among the thermolysis products of the phenylazo derivative (**1f**).



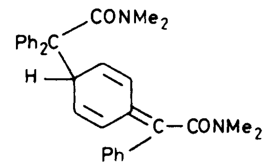
(**1**)
a; X = Br
b; X = Cl
c; X = H
d; X = OMe
e; X = OH
f; X = N=NPh
g; X = CH_2OH



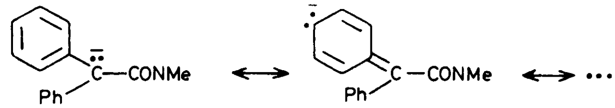
(**2**)
a; $n = 0$
b; $n = 1$
c; $n > 1$



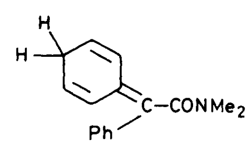
(**3**)



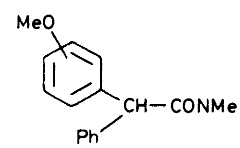
(**4**)



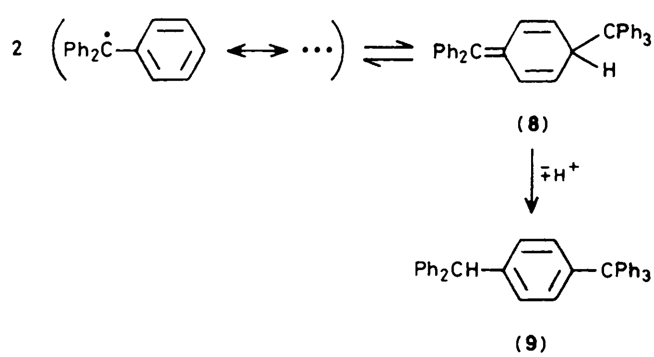
(**5**)



(**6**)



(**7**)
(*ortho* and *para*)



Moreover, treatment with base (or acid) of equilibrium mixtures of trityl radicals and their dimer (**8**)[9] [structurally related to compound (**4**)] furnishes solely the fully aromatic isomer (**9**)[9b] [structurally related to dimer (**2a**)], without trimeric products having, to our knowledge, been isolated as additional products in these reactions.

Table 1. Reaction of 2-bromo-2,2-diphenylacetamide (**1a**) with sodium methoxide in 2,2-dimethoxypropane (DMP) at room temperature; the effect of added acetone

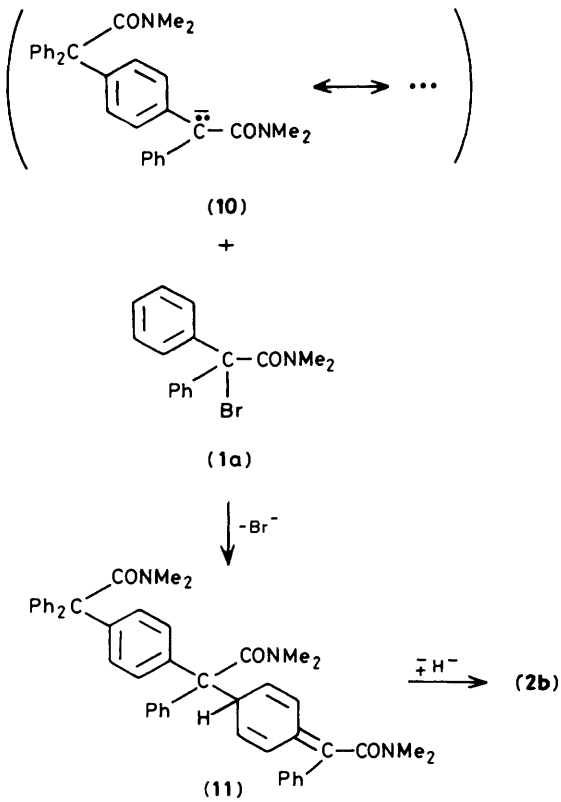
	(**1a**) (g; mmol)	NaOMe[a]	DMP[b,c]	Acetone[a]	Reaction time	Method of work-up[c]	Products and yields, (%)[d] (**1c**)	(**2a**)	(**2b**)	(**2c**)	(**1d**)	(**1e**)	(**7**)	Total
1	0.5 1.57	4.0	10		4 days	A	5	10	4	7	27	11	18	82
2	0.5 1.57	4.0	10		2 h	A	*f*	*f*			62[g]	*f*		>62
3	0.5 1.57	4.0	10	1	2 h	B	55	24[h]						79
4	0.5 1.57	4.0	10	2	2 h	B	60	27[h]						87
5	0.5 1.57	4.0	10	3	2 h	B	65	19[h]						84
6	2.0 6.28	4.0	10	0.3	3 days	B	45	32	13					90
7	6.0 18.84	4.0	10	0.3	5 days	B	31.5	27	8			5		71.5
8	0.5 1.57	4.0	10	0.1	5 days	B				50		13		63

[a] mmol per mmol (**1a**). [b] ml per g (**1a**). [c] See Experimental section. [d] Yields of isolated products. [e] Refluxed for 4 h and freshly distilled from $LiAlH_4$; acetone-free. [f] Detected by t.l.c., not isolated. [g] Mostly formed from unchanged starting material during work-up, see text. [h] Practically no other products were formed (t.l.c.).

On the other hand, the base-induced rearrangement of the (non-isolated) intermediate (**4**) into the stable dimer (**2a**) (*cf.* Scheme 1) requires the intermediacy of the anion (**10**) which, rather than abstract a proton, could react with a molecule of unchanged starting substance (**1a**) to furnish the trimer by what we call the carbanionic mechanism of trimer formation. Assuming that the monomeric and dimeric units of the trimer may become linked solely through their α and/or *para* carbon atoms [as is the case in the dimer (**2a**), and which appears to be highly probable according to the ^{13}C n.m.r. spectrum], four alternative structures, among them structure (**2b**), may be drawn for the trimer. The suggested mechanism of the reaction is shown, for the formation of (**2b**), in Scheme 2. This mechanism appears to be all the more reasonable because formation of significant amounts of the trimer takes place only when the initiation step [equation (1a)], because of the low concentration of acetone, is inefficient, which means that the rate of the entire process is considerably reduced and therefore, at the moment of formation of the dimeric anion (**10**), the starting compound (**1a**) is still present in sufficiently high concentration. A further factor favouring trimer formation is that, because of the slight amount of added acetone, the concentration of proton sources (acetone itself and/or the methanol originating from the reaction of acetone with methoxide) in the mixture is low and therefore protonation of the anions (**10**) is retarded.

Among the four alternative structures only one, (**2b**), is in agreement with the ^1H and ^{13}C n.m.r. spectra, according to which the trimer contains (i) a single hydrogen atom attached to saturated carbon, (ii) two quaternary carbon atoms, and (iii) seven different types of non-equivalent aromatic carbon atoms bearing no hydrogen.

In the ^1H n.m.r. spectrum the *N*-methyl groups of the trimer give rise to two groups of signals at δ *ca.* 2.3 and 3.0, respectively, their intensity ratio being 1:2. This, too, is in agreement with structure (**2b**) because, according to the latter, the trimer contains one *NN*-dimethyl-2,2-diarylacetamide and two *NN*-dimethyl-2,2,2-triarylacetamide moieties, and the *N*-methyl signal of *NN*-dimethyl-2,2-diphenylacetamide is known to appear at δ 3.0 (s), while the *N*-methyl groups of



Scheme 2.

NN-dimethyl-2,2,2-triphenylacetamide give rise to two groups of signals (both broad) of equal intensity at δ 2.35 and 3.05.[3]

The mechanism of formation of the oligomers (**2c**) should be analogous to that of the trimer. In agreement with this assumption the formation of the oligomers becomes predominant when the amount of added acetone is further reduced. The

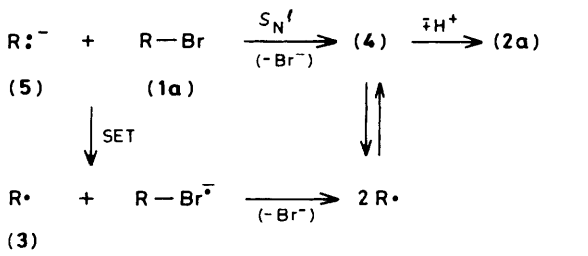
average degree of oligomerization of the product isolated in one of our experiments (Table 1, entry 8) was calculated on the basis of the intensity ratio 3:4 of the two groups of *N*-methyl signals at δ 2.30 and 2.98, respectively, to be $n + 2 = 7$ (see above).

In summary S_N and SET pathways compete when the bromo derivative (**1a**) is allowed to react with sodium methoxide in acetone-free DMP. Generation of acetone enolate (which is a more efficient single-electron donor than methoxide ions) in the reaction mixture completely suppresses the S_N reactions of compound (**1a**). In the presence of small amounts of acetone enolate the main SET product is a mixture of oligomers (**2c**) which, when the amount of acetone enolate is increased, becomes replaced first by mixtures of the trimer (**2b**), the dimer (**2a**), and the reduction product (**1c**) and, subsequently, by mixtures of the dimer (**2a**) and the reduction product (**1c**). This variation of the product composition is in agreement with the operation of the carbanionic mechanism of trimer and oligomer formation.

The establishment of the carbanionic mechanisms of trimer and oligomer formation necessitated the reconsideration of the mechanism of dimer formation. A deuterium tracer study has namely shown[1] that hydrogen abstraction by the radicals (**3**) may lead, in addition to compound (**1c**) [Scheme 1, equation (3)], to the formation of cyclohexadiene-type isomers of the latter, *e.g.* to compound (**6**) [equation (3a)], which subsequently rearrange into compound (**1c**) by a deprotonation–protonation mechanism, *i.e. via* the monomeric anion (**5**). If the dimeric anion (**10**) is able to react with unchanged starting compound (**1a**) to furnish intermediate (**11**) and then trimer (**2c**) (Scheme 2) (as is indeed the case), the monomeric anion (**5**) and a molecule of unchanged starting compound should similarly furnish compound (**4**) and, by rearrangement of the latter, the dimer (**2a**) (Scheme 3).*

Formation of the dimer (**2a**) by the carbanionic mechanism may be envisaged as a simple S_N' reaction. However, considering that the carbanion (**5**) might, similarly to the enolate of acetone, be capable of transferring an electron to the bromo derivative (**1a**), the possibility of the formation of intermediate (**4**) by an SET-initiated process exists, *i.e.* there exist two distinct versions of the carbanionic mechanism of dimer [and similarly of trimer] formation (Scheme 3). At present there appears to be no reliable method of differentiating between the two versions. However, in view of the S_N' reaction of compound (**1a**) with methoxide being rather slow (see above), the SET version of the carbanionic mechanism of dimer formation appears to be more likely. In any case, when talking about the carbanionic mechanism of dimer formation, either or both of these versions (S_N' and SET) are meant. The carbanionic mechanism has to be envisaged as an additional mechanism rather than as an alternative to dimer formation by recombination [equation (5), Scheme 1] since the radicals (**3**) generated by thermolysis of the phenylazo derivative (**1f**), *i.e.* under conditions where, because of the absence of the bromo derivative (**1a**), the carbanionic mechanism may not operate, also furnish the dimer (**2a**).[4,5]

The operation of the carbanionic mechanism of dimer formation in a special case has been established with the aid of a crossing experiment (see below).



Scheme 3.

Establishment of the Chain Nature of the Title Reaction.—Perhaps the most characteristic feature of the title reaction is the *non-formation* of the hydroxymethyl derivative (**1g**) (neither at ambient nor at reflux temperatures) while thermolysis of the phenylazo derivative (**1f**), which involves the intermediacy of the same radicals (**3**), furnishes ample amounts of compound (**1g**) in addition to the products (**1c**) and (**2a**) of the title reaction.[4,5] Formation of the hydroxymethyl derivative (**1g**) in the thermolysis experiments may be assumed to take place *via* the two-step sequences (3) + (7a), (3a) + (7a), (3b) + (7b), and/or (3c) + (7c) (Scheme 1) (with subsequent protonation during work-up and hydrolysis in the first and last two cases, respectively). The non-formation of this compound in the title reaction therefore indicates rapid consumption of the radical anions $^{\bullet}CH_2O^-$ and/or the radicals $^{\bullet}CH_2OY$ and $^{\bullet}CH_2OH$ by the bromide (**1a**), the only species present in the reaction mixtures of the title reaction but absent from the thermolysis mixtures. [A further such species is the bromide anion. However, bromide anions have no effect on the formation of the hydroxymethyl derivative (**1g**), as shown by the observation that the phenylazo derivative (**1f**), when refluxed with DMP in the presence of lithium bromide, furnished, among other products, 18% of the hydroxymethyl derivative (**1g**) while, in the absence of lithium bromide, 14—22% of this product were obtained.] Reactions (4), (4a), and (4b) of Scheme 1 were tentatively considered as possible candidates for the explanation of the scavenging effect of bromide (**1a**). However, reactions (4a) and (4b) could be of only minor importance since, because of the charge separation involved, their rate is probably not high enough. This does not apply to reaction (4) and, since several examples were known from literature[10–12] for SET from the $^{\bullet}CH_2O^-$ radical anion to organic halides, reaction (4) was assumed to be the crucial cause of the non-formation of the hydroxymethyl derivative (**1g**) in the title reaction.[4] As a consequence, it had furthermore to be assumed either that, among the hydrogen abstraction reactions, (3) and (3a) are the major while reactions (3b) and (3c) are at most minor pathways, or that the radicals resulting from the latter two reactions are rapidly converted into $^{\bullet}CH_2O^-$ radical anions [equations (8a) and (8b), respectively]. In any case, the non-formation of the hydroxymethyl derivative (**1g**) in the title reaction was considered as indirect evidence in favour of the chain mechanism of the conversion (**1a**)→(**1c**).† However, the assumed role of bromide (**1a**) in preventing formation of the hydroxymethyl derivative (**1g**) was not proved.[4] Moreover, a recent deuterium tracer study has shown that the $^{\bullet}CH_2OY$ radicals, rather than the radical anions CH_2O^- (and the radicals $^{\bullet}CH_2OH$), are the main sources of the hydroxymethyl derivative (**1g**) in the thermolysis of the phenylazo derivative

* A further pathway of formation of the carbanions (**5**), *viz.* the one-electron reduction by acetone enolate of the radicals (**3**) [reaction (6a), Scheme 1] appears to be of lesser importance for the operation of the carbanionic mechanism of dimer formation because reaction (6a) becomes efficient only in the presence of a large excess of acetone (see above), *i.e.* under conditions when the starting bromide (**1a**) is rapidly consumed [reaction (1a)]. Therefore the carbanions (**5**) resulting from reaction (6a) are mostly protonated to give the reduction product (**1c**). For carbanion (**5**) formation by deprotonation of the reduction product (**1c**), see below.

† For the participation of the formaldehyde radical anion as a chain carrier in the dehalogenation of aryl and heteroaryl halides, see refs. 10—12; for a similar role for the thioformaldehyde radical anion in the denitration of an alicyclic nitro derivative, see ref. 13.

Table 2. Thermolysis of the 2,2-diphenyl-2-phenylazoacetamide (**1f**) in 2,2-dimethoxypropane (DMP) in the presence of the 2-bromo-2,2-diphenylacetamide (**1a**)

	(**1f**) (g; mmol)	(**1a**) (g; mmol)	NaOMe[a]	DMP[b,c]	Reaction conditions–work-up[d]	Reaction time (h)	Products and yields (%)[e] (**1f**)	(**1g**)	(**2a**)	(**2b**)	(**2c**)	(**1d**)[f]	(**1e**)[f]	Total
1[g]	1.0 2.9		4.0	10	A–F	5	20	17	16					53
2[g]	0.52 1.5		4.0	30	B–F	4	8	25	8					41
3[h]	0.52 1.5	0.48 1.5	8.0	60	B–D	5	*i*	*i*	39 42	9 8	*k*		*k*	48[l] 50[l]
4	0.52 1.5	0.48 1.5		60	C[m]–F	7	16	2.7				29	15	63
5	0.05 0.15	0.46 1.46	4.0[n]	10[p]	A–E	1		*q*	14	6	54	8	6	88
6	0.11 0.31	0.5 1.57	4.0[n]	10[p]	A–D	5	Traces	*q*	23	8.5	25			56.5

[a] mmol per mmol (**1f**). [b] ml per g (**1f**). [c] Refluxed for 6 h with and freshly distilled from $LiAlH_4$; acetone-free. [d] See text. [e] Yields of isolated products; for compounds (**1d**)[f] and (**1e**)[f] based on the amount of the bromide (**1a**), for compound (**1g**) on the amount of the phenylazo derivative (**1f**), for all other products on the sum of the amounts of compounds (**1a**) and (**1f**) introduced. [f] Formed during work-up from unchanged bromide (**1a**). [g] Ref. 1. [h] Two identical runs. [i] Not detectable by t.l.c. [k] Traces detected by t.l.c. [l] Further non-identified products were detected by t.l.c. [m] In the absence of NaOMe. [n] mmol per mmol (**1a**). [p] ml per g (**1a**). [q] Irrelevant because of the minute amount of compound (**1f**) introduced.

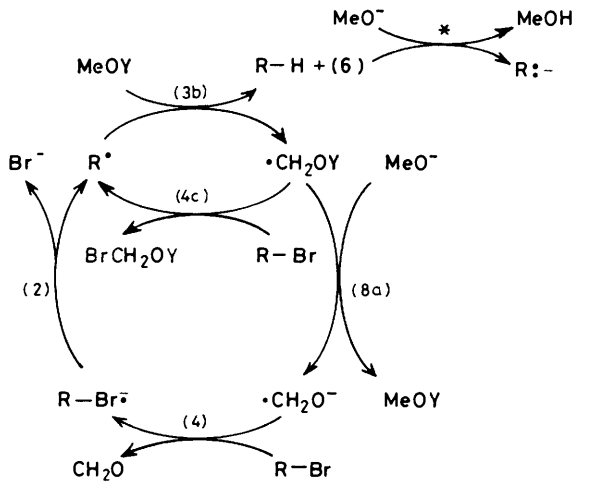
(**1f**).[1] It was therefore felt important to prove unambiguously the role of bromide (**1a**) in preventing formation of the hydroxymethyl derivative (**1g**).

If it is indeed the bromide (**1a**) which prevents formation of the hydroxymethyl derivative, it should do so irrespective of the source of the radicals (**3**). Therefore, the addition of compound (**1a**) to the thermolysis mixture of compound (**1f**) should result in a decrease of the yield of compound (**1g**) or even its complete disappearance from the product mixture. When an equimolar mixture of the bromo (**1a**) and phenylazo derivatives (**1f**) was slowly added to a refluxing suspension of sodium methoxide in acetone-free DMP, not even traces of the hydroxymethyl derivative (**1g**) were formed (Table 2, entry 3). That the non-formation of the latter is the result of the presence of the bromide (**1a**) rather than of the slow addition becomes evident from a comparison of entries 1 and 2: in the absence of the bromide (**1a**) the hydroxymethyl derivative (**1g**) *is* formed from the phenylazo derivative (**1f**) irrespective of the rate of addition of the latter.

Since the $^{\bullet}CH_2OY$ radicals rather than the radical anions $^{\bullet}CH_2O^-$ (and the radicals $^{\bullet}CH_2OH$) are the main sources of the hydroxymethyl derivative (**1g**) in the thermolysis experiments, reaction (4) may be only partly responsible for the non-formation of compound (**1g**) in the title reaction. In other words, bromide (**1a**) must be able to scavenge the $^{\bullet}CH_2OY$ radicals as well.

How could the bromide (**1a**) effect this and thereby prevent the recombination reaction (**7b**) occurring? Since reaction (4a) had to be rejected as the explanation (see above), we believe that the scavenging effect of the bromo derivative (**1a**) is instead mainly based on the bromine abstraction reaction (4c). This view is supported by the observation that only slight amounts of the hydroxymethyl derivative (**1g**) were obtained when the phenylazo derivative (**1f**) was slowly added to a refluxing solution of an equimolar amount of the bromide (**1a**) in acetone-free DMP in the *absence* of sodium methoxide (Table 2, entry 4).

Since the simultaneous presence of bromide (**1a**) and sodium methoxide *completely* prevents formation of compound (**1g**) in the thermolysis of the phenylazo derivative (**1f**) whereas the presence of solely the bromide (**1a**) in the thermolysis mixture results only in a sharp decrease of the yield of compound (**1g**) (Table 2, entries 3 and 4), the operation of some other factor or factors has to be assumed in the presence of sodium methoxide



Scheme 4. The numbers on the arrows refer to the reactions listed in Scheme 1. * Methoxide and methanol may be replaced by acetone enolate and acetone, respectively.

in addition to the operation of reaction (4c). The following factors may be thought to be responsible for the difference mentioned: (i) in the presence of sodium methoxide hydrogen abstraction reactions (3) and (3a) compete to some extent with reaction (3b),[1] *i.e.* less $^{\bullet}CH_2OY$ is formed; (ii) only in the presence of sodium methoxide does reaction (8a) operate at all and contribute to the consumption of radicals $^{\bullet}CH_2OY$ to some extent [although, under the conditions of the thermolysis of the phenylazo derivative (**1f**) in the *absence* of bromide (**1a**), reaction (8a) has been shown to be inefficient.[1]]

These observations indicate that it is indeed the bromide (**1a**) which prevents recombination of the radicals R• = (**3**) [irrespective of whether their source was the bromide (**1a**) itself or the phenylazo derivative (**1f**)] with the radical anion $^{\bullet}CH_2O^-$ and the radicals $^{\bullet}CH_2OY$ (and $^{\bullet}CH_2OH$) by rapidly scavenging them; in other words that formation of compound R–H = (**1c**) [as well as of the isomeric compound (**6**)] indeed take place *via* chain processes, see *e.g.* the propagation cycles depicted in Scheme 4. Deprotonation of the cyclohexadiene (**6**) to the anion $R:^-$ = (**5**) is clearly an extra-chain process neither requiring

intervention of a chain-carrier, nor destroying one. The anion is subsequently either protonated to furnish the reduction product (**1c**) or reacts with a molecule of unchanged bromide (**1a**) to furnish dimer (**2a**) (Scheme 3). All these processes are clearly extra-chain processes, as are also those leading to the formation of trimer (**2b**) (Scheme 2) and oligomers (**2c**). Therefore neither of the processes leading to products (**1c**), (**2b**), and (**2c**) does interfere, by consumption of a chain carrier without generating simultaneously a new one, with the propagation cycle, nor does, in contrast to the formation of the dimer (**2a**) by radical recombination [Scheme 1, equation (5)], dimer formation by the carbanionic mechanism.

This removes the vulnerable point of the originally suggested mechanism,[4] according to which the dimeric product (**2a**) is formed *exclusively via* radical recombination and which therefore failed to explain the comparable yields of the reduction product (R–H) = (**1c**) and the dimer (**2a**).

A further peculiarity of the thermolyses of the phenylazo derivative (**1f**) carried out in the simultaneous presence of the bromide (**1a**) and sodium methoxide (Table 2, entries 3 and 5—7), *viz.* the non-formation or the formation of only traces of the reduction product (**1c**), will be discussed below.

Further support in favour of the chain mechanism of the title reaction came from a study of the effect of the phenylazo derivative (**1f**) on the reactivity of bromide (**1a**) when mixtures of these two compounds were refluxed in DMP in the presence of sodium methoxide. The presence of 0.2 mol. equiv. or more of the phenylazo derivative (**1f**) results in significant increase of the rate of disappearance of bromide (**1a**) as shown by our failure to isolate the *ipso*-substitution products (**1d** and **e**) (which would be formed during work-up from unchanged starting bromide) in these experiments; furthermore, the yield of the oligomeric fraction (**2c**) decreases with increasing amounts of the phenylazo derivative (**1f**) (Table 2, entries 3 and 6). Since the decrease of the yield of the oligomers (**2c**) [with simultaneous increase of the total yield of the other SET products (**1b**), (**2a**), and (**2b**)] points to increasing effectiveness of initiation, these observations appear to indicate that the radicals R$^{\bullet}$ = (**3**), generated by thermolysis of the phenylazo derivative (**1f**), are able to initiate the conversion of bromide (**1a**) into its SET products.

The Effect of Temperature Elevation on the Title Reaction, and Establishment of the Operation of the Carbanionic Mechanism of Dimer Formation in a Special Case.—The study of the temperature effect on the title reaction was required for the justification of the comparison of the title reaction (originally conducted at ambient temperatures[4]) with the thermolysis of the phenylazo derivative (**1f**), both reactions involving the intermediacy of the radicals (**3**).

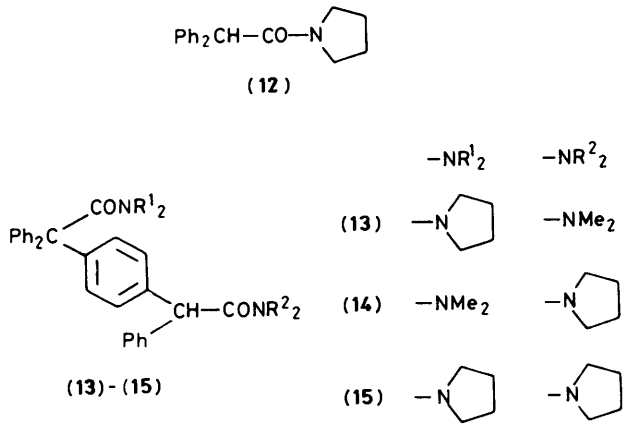
While elevation of the reaction temperature to the b.p. accelerated the reaction considerably but had no significant effect on product composition when the reaction was carried out in the presence of acetone (compare Table 3, entry 1, with Table 1, entries 6 and 7), it caused significant changes both in the product composition and the reaction rate when the reactions were carried out in the absence of acetone (compare Table 3, entry 2, with Table 1, entry 1). The most conspicuous differences in the product composition are the sharp drop of the yield of both (i) the reduction product (**1c**) and (ii) the *tele*-substitution products (**7**)[2,5] with (iii) simultaneous considerable increase (from 26 to 57%) of the *total* yield of the SET products [(**1c**), (**2a**—**c**), the oligomers (**2c**) becoming the main products] as a result of temperature elevation.

The non-formation of the reduction product (**1c**) [*cf.* above with similar observations in the thermolyses of mixtures of compounds (**1a** and **f**) in the presence of sodium methoxide], and the considerable increase in the yield of the oligomers (**2c**) at reflux temperature in the absence of acetone may be rationalized by assuming that any product (**1c**) primarily formed [from radicals (**3**) by hydrogen abstraction] is rapidly deprotonated at elevated temperatures to the carbanions (**5**) which react with unchanged starting bromo derivative (**1a**) to furnish successively the dimer (**2a**) (Scheme 3), the trimer (**2b**) (Scheme 2), and the oligomers (**2c**). The effect of the addition of acetone on product composition is also readily understood on the basis of this assumption. Although, as shown by a deuterium tracer study,[1] reversible formation of the carbanions

Table 3. Reaction of 2-bromo- (**1a**) and 2-chloro-*NN*-dimethyl-2,2-diphenylacetamide (**1b**) with sodium methoxide in refluxing 2,2-dimethoxypropane (DMP)

	Starting compound	(g; mmol)	NaOMe[a]	DMP[b,c]	Acetone[a]	Reaction time (h)	Method of work-up[d]	Products and yields (%)[e] (1c)	(2a)	(2b)	(2c)	(1d)	(1e)	Total
1	(**1a**)	0.5 1.57	4.0	10	0.3	3	C	27	36	10	2		20	95[f]
2	(**1a**)	0.5 1.57	4.0	10		5	C		5	5	47[g]	7[h]	8	72
3	(**1b**)	1.0 3.66	4.0	10		6	A					93[i]		93[h]
4	(**1b**)	1.0 3.66	4.0	10	0.28	20	A	7			33	33	9	82
5	(**1b**)	1.0 3.66	4.0	10	1	6	C	10	23	10	9		*k*	52
6	(**1b**)	1.0 3.66	4.0	10	2	6	C	14	28	11			*k*	53
7	(**1b**)	1.0 3.66	4.0	10	3	6	A	23	24	3				50

[a] mmol per mmol (**1a**) and (**1b**), respectively. [b] ml per g (**1a**) and (**1b**), respectively. [c] Refluxed for 6 h with and freshly distilled from $LiAlH_4$; acetone-free. [d] See Experimental section. [e] Yields of isolated products. [f] A similar product mixture resulted when the reaction was carried out in DMP which had not been pretreated with $LiAlH_4$, *i.e.* which was contaminated with acetone. [g] The ^1H n.m.r. spectrum of the oligomer exhibited a very weak signal at δ 3.7 indicating the presence of methoxy groups attached to the *para* or *ortho* positions of one of the terminal phenyl rings of some molecules. For the significance of this observation, see text. [h] At most, traces of the *tele*-substitution products (**7**)[2] were present in the product mixture. [i] Formed during acidification with methanolic HCl (the first step of the work-up procedure); not present (t.l.c.) in the original reaction mixture. [k] Traces detected by t.l.c. A further product of unknown structure was also detected.



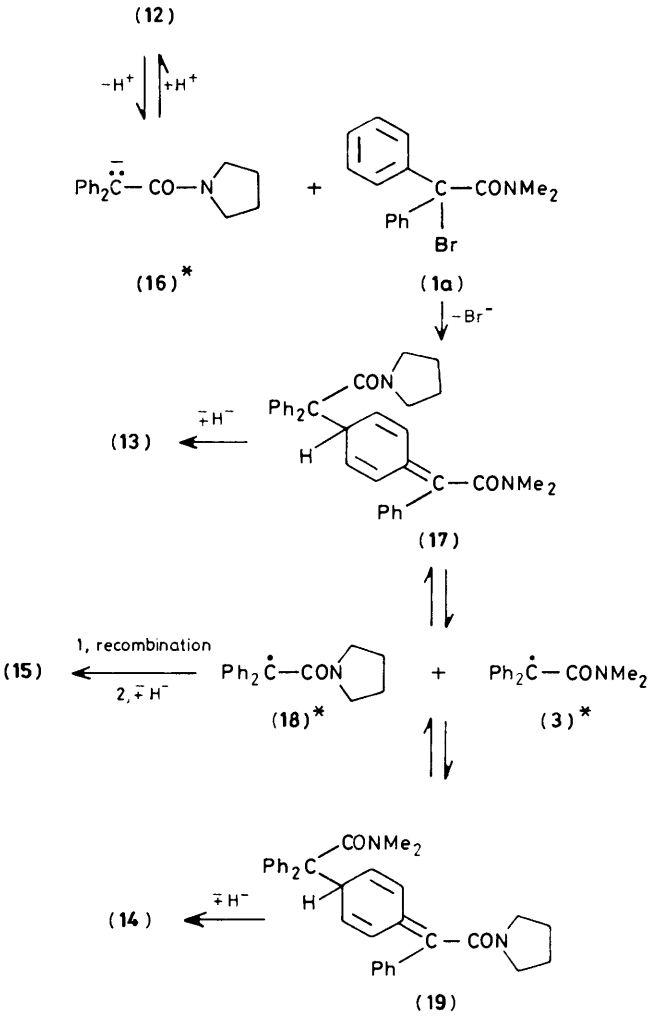
(5) takes place when compound (**1c**) is treated with sodium methoxide in DMP–acetone mixtures, deprotonation of compound (**1c**) should be suppressed by acetone and/or methanol (resulting from the reaction of acetone with methoxide anions) as proton sources. Furthermore, because of the much greater efficiency of initiation step (1a) relative to initiation step (1), in the presence of acetone the bromo derivative (**1a**) is consumed considerably faster. Both effects should result in decreased yields of products (**2a**—**c**), and especially of the oligomers (**2c**), as was indeed the case (compare experiments 1 and 2, Table 3).

It is to be noted that significant amounts of the reduction product (**1c**) result from the thermolysis of the phenylazo derivative (**1f**) in DMP even in the presence of sodium methoxide[1] since, in the absence of the bromo derivative (**1a**), the carbanions (**5**) may not be trapped in the form of compounds (**2a**—**c**) in this case. This observation, therefore, may be considered as supporting the validity of the carbanionic mechanisms of dimer, trimer, and oligomer formation.

In order to check the hypothesis that at elevated temperatures the reduction product (**1c**) is, at least in the absence of acetone, deprotonated to the carbanions (**5**), compound (**1a**) was treated with sodium methoxide in refluxing acetone-free DMP in the presence of *N*-(2,2-diphenylacetyl)pyrrolidine (**12**).[3] The dimeric fraction of the product mixture was found to contain, in addition to compound (**2a**), the mixed dimers (**13**) and (**14**) as well as the dimer (**15**) which, under the conditions of the chromatographic work-up procedure used, are not separated from each other.[3] However, a comparison of the ^{1}H n.m.r. spectrum of the dimeric fraction with the spectra[3] of the four authentic dimers proved the presence of both *N*-di- and *N*-triarylacetylpyrrolidine groups; the mass spectrum revealed the presence of the two simple dimers (**2a**) and (**15**)[3] ($M^{+\cdot}$ = *m*/*z* 476 and 528, respectively) as well as of one or both of the mixed dimers (**13**)[3] and (**14**)[3] ($M^{+\cdot}$ = *m*/*z* 502), *i.e.* incorporation of the pyrrolidide (**12**). This may be rationalized on the basis of the mechanism depicted in Scheme 5. The formation of the dimer (**15**) demonstrates that the rearrangement of intermediate (**17**) into the dimer (**13**) is not so fast as to prevent its dissociation into radicals (**18**) and (**3**). As a consequence, *both* mixed dimers, (**13**) and (**14**), must be present.

The key step is the reaction of the carbanion (**16**) with one molecule of the unchanged starting compound (**1a**) which is analogous to the reaction of carbanions (**5**) with the latter, leading ultimately to the formation of the simple dimer (**2a**) (Scheme 2).

By the incorporation of the pyrrolidide (**12**) into the resulting dimers a special version of the carbanionic mechanism of dimer formation is only proved, that in which the carbanions result by deprotonation of the corresponding diphenylacetamide. The



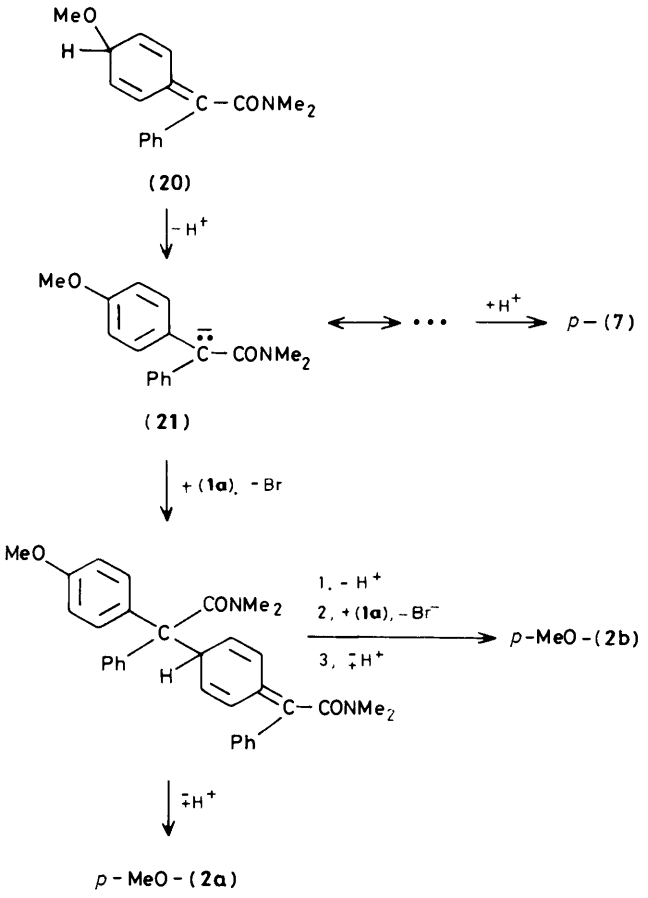
Scheme 5.†

* Only one limiting structure is shown. † Formation of the reduction product (**1c**) from (**3**) and the analogous conversion (**18**)→(**12**) are not shown.

crossing experiment discussed is not suited for proving (or disproving) the more general version of the carbanionic mechanism of dimer formation where the carbanions result by one-electron reduction of the corresponding radicals [Scheme 1, reaction (6)].

When the same crossing experiment was repeated at room temperature in the presence of three mol. equiv. of acetone,* the resulting dimeric fraction proved to contain exclusively the dimer (**2a**) (^{1}H n.m.r.), similarly to the dimeric fraction resulting from a crossing experiment carried out earlier[3] in DMP which had not been pretreated with LAH, *i.e.* which was contaminated by acetone. We believe that incorporation of the pyrrolidide (**12**) into the resulting dimer in the crossing experiments conducted in the presence of acetone at ambient temperature is partly prevented by the same factors which tend to suppress formation of the simple dimer (**2a**), the trimer (**2b**), and the oligomers (**2c**) in the presence of acetone, and partly by the decreasing tendency of carbanions (**16**) to be formed by deprotonation of compound (**12**) and/or to react with

* In the absence of acetone the reaction was too slow at room temperature to permit a meaningful result to be obtained.



Scheme 6.

unchanged bromide (**1a**) as the reaction temperature is lowered, as has been observed for the related carbanion (**5**) (compare Table 3, entry 2, with Table 1, entry 1).

The *tele*-substitution products (**7**) are known to be the products of S_N' reactions of compound (**1a**) and to involve, as shown for the *para*-derivative in Scheme 6, rearrangement by deprotonation–protonation of the primary products (**20**) and its *ortho* isomer, respectively, to the final products.[5] The formation of only trace amounts of these products at elevated temperatures in the absence of acetone (Table 2, entry 2) may, therefore, be the result of either the non-formation of intermediate (**20**) and its *ortho* isomer, or of the anion (**21**) and its *ortho* isomer reacting predominantly with unchanged starting compound (**1a**) rather than being protonated. The reaction with compound (**1a**) should be favoured by the absence of acetone [for the same reasons as explained above for the reaction of the carbanion (**5**) with compound (**1a**)] and lead to the formation of methoxylated dimers, methoxylated trimers (see Scheme 6), and methoxylated oligomers. The oligomeric fraction (**2c**) has been shown by its ^{1}H n.m.r. spectrum to be indeed contaminated by methoxylated oligomers. However, the intensity of the methoxy signal was very low. Therefore the main reason of the formation of only trace amounts of the *tele*-substitution products (**7**) must be the negligible relative rates of formation of intermediate (**20**) and of its *ortho* isomer, *i.e.* that by elevation of the reaction temperature the ratio of S_N and SET processes is altered in favour of the latter.*

* This implies also that the two *ipso*-substitution products (**1d** and **e**) (experiment 2, Table 3) are formed during work-up from unchanged starting material (see above).

Effect of the Replacement of Bromine by Chlorine.—In contrast to the bromo derivative (**1a**) (Table 3, entry 2) the chloro analogue (**1b**) does not react with sodium methoxide in acetone-free DMP even at reflux temperature, and the unchanged starting compound was converted into the methanolysis product (**1d**) when treated with methanolic hydrogen chloride during work-up (Table 3, entry 3). That this *ipso*-substitution product was formed during work-up rather than in the course of the reaction is again shown by the non-formation of the *tele*-substitution products (**7**). Addition of increasing amounts of acetone caused the formation of variable amounts of the SET products (**1c**) and (**2a—c**). While the amount of the reduction product (**1c**) steadily increases, the amounts of the dimer, the trimer, and the oligomers (**2a—c**) reach a maximum and subsequently decrease with increasing amounts of added acetone (Table 3, entries 4—7).

All this may be explained by assuming that the mechanism derived for the SET-initiated reactions of bromide (**1a**) apply, in a qualitative sense, to the reactions of the analogous chloride as well, although some quantitative differences in the final outcome of the reactions result from the replacement of bromine by chlorine. For example SET from methoxide to the chloro derivative (**1b**) does not take place even at elevated temperatures but the enolate of acetone is an effective single-electron donor also towards compound (**1b**).

In general, the chloro analogue (**1b**) appears to be less reactive in SET reactions than its bromo analogue; a similar decrease of the overall reactivity of the halogenobenzenes in $S_{RN}1$ reactions (which constitute an important class of SET-initiated reactions) with decreasing mass number of the halogen has been observed earlier.[7]

Experimental

Fourier transform ^{1}H and ^{13}C n.m.r. spectra were recorded with a JEOL FX-100 spectrometer in $CDCl_3$ solutions, using Me_4Si as internal reference; i.r. spectra were obtained with a Spektromom 2000 instrument (Hungarian Optical Works, Budapest). Mass spectra were recorded with an AEI MS-902 spectrometer at 70 eV, using the direct inlet system. Kieselgel 60 $PF_{254+366}$ was used as the adsorbent in t.l.c. and benzene–acetone (8:2 when small, and 7:3 when large, amounts of dimers and oligomers were present) as the solvent.

Solvent DMP (purchased from EGA-Chemie; 98% purity) was purified by refluxing for 6 h with excess of $LiAlH_4$; before use it was freshly distilled from $LiAlH_4$.

Reaction of 2-*Bromo*-NN-*dimethyl*-2,2-*diphenylacetamide* (**1a**) *with Sodium Methoxide at Room Temperature.*—Compound (**1a**) was stirred with a suspension of sodium methoxide in acetone-free DMP or mixtures of acetone-free DMP and acetone at room temperature; for details, see Table 1. The resulting mixtures were worked up according to one of the following methods.

Method A. The mixture was acidified with methanolic HCl and evaporated to dryness. The residue was taken up in and refluxed with methanol. The solution was evaporated again and the residue was taken up in CH_2Cl_2 and water. The CH_2Cl_2 layer was dried ($MgSO_4$), evaporated to dryness, and worked up by preparative t.l.c. [This method was applied mostly in those cases where considerable amounts of the starting substance (**1a**) remained unchanged, in order to convert the latter into its methanolysis product (**1d**).]

Method B. The mixture was evaporated to dryness. Water was added and the mixture was acidified with acetic acid, extracted with CH_2Cl_2, and worked up as in Method A.

Method C. This was the same as Method B, but HCl was used rather than acetic acid for acidification.

The known products [(**1c**),[2,3,14] (**1d**),[2,3] (**1e**),[15] (**2a**),[2,3] and (**7**)[2]] were identified by comparison of their R_F values and i.r. spectra with those of authentic samples. In those experiments in which larger amounts of the dimer were obtained the ^1H n.m.r. spectrum of the product was also compared with that of an authentic sample. The i.r. spectra of the dimer (**2a**), the trimer (**2b**), and the oligomers (**2c**) were practically identical; however, the ^1H n.m.r. spectra (the intensity ratio of the two groups of *N*-methyl signals, see above) as well as the R_F values of these products were different. The R_F value of the trimer is smaller than that of the dimer. All fractions migrating more slowly than the trimer (including the non-migrating fractions; $R_F = 0$), *i.e.* the oligomers (**2c**) differing in their degree of oligomerization, were combined. The trimer and the oligomers, obtained by precipitation from their methanolic solutions with water, are amorphous substances (possibly mixtures of diastereoisomers) with no sharp m.p.s.

Trimer, δ_H 2.31 (6 H, m) + 2.98 (12 H, s) (N-Me), 5.14 (1 H, s, ⩾C–H), and 7.0—7.3 (28 H, m, ArH); δ_C* 36.1 + 37.5 (NMe of *NN*-dimethyl-2,2-diarylacetamide moiety), 37.5 + 39.5 (*N*Me of *NN*-dimethyl-2,2,2-triarylacetamide moieties), 54.1 (d, ⩾CH), 66.6 (s) + 66.9 (s) (–C–), 126.4 (d), 127.6 (d), 128.3 (d), 128.5 (d), 128.9 (d), 129.4 (d), 130.0 (d), 137.4 (s), 137.9 (s), 139.1 (s), 141.1 (s), 141.4 (s), 141.8 (s), and 142.9 (s) (aromatic C), 171.6 (C=O of *NN*-dimethyl-2,2-diarylacetamide moiety), and 172.6 p.p.m. (C=O of *NN*-dimethyl-2,2,2-triarylacetamide moieties); *m/z* (230 °C) 713 ($M^{+\cdot}$, 3%), 641 (70), 569 (30), 497 (29), 404 (36), 383 (13), 222 (21), and 72 (100).

Oligomers (**2c**) (Table 1, entry 8), δ_H 2.30 (s) + 2.98 (s) (intensity ratio 3:4, NMe), 5.14 (s, very weak, ⩾C–H), and 7.0—7.25 (m, ArH).

Thermolysis of the 2,2-*Diphenyl*-2-*phenylazoacetamide* (**1f**) *in DMP in the Presence of the* 2-*Bromo*-2,2-*diphenylacetamide* (**1a**).—Mixtures of compounds (**1a** and **f**) (or, for comparison, the individual compounds) were refluxed with the suspension of sodium methoxide in acetone-free DMP (refluxed for 6 h with and freshly distilled from $LiAlH_4$) with continuous stirring (Method A); alternatively, mixtures of compounds (**1a** and **f**) [or, for comparison, the individual compound (**1f**)] were added in small portions at intervals of 10 min within 4 h to the refluxing suspension of sodium methoxide in acetone-free DMP with continuous stirring, and the mixture was refluxed for another 1 h (Method B); or compound (**1f**) was added in small portions at intervals of 10 min within 4 h to the refluxing solution of compound (**1a**) in acetone-free DMP, and the mixture was refluxed for a further 3 h; methanol (5 ml) was added and refluxing was continued for 1 h (Method C). For details, see Table 2. The resulting mixtures were subsequently evaporated to dryness; water was added and the mixtures were acidified with HCl and extracted with CH_2Cl_2. The CH_2Cl_2 solutions were dried ($MgSO_4$), evaporated to dryness, and worked up by preparative t.l.c. (Kieselgel 60 $PF_{254+366}$; benzene–acetone, 8:2 or 7:3, depending on whether small or large amounts of dimers and oligomers were present) (Method D). Alternatively, the reaction mixtures were acidified with methanolic HCl and evaporated to dryness; the residues were taken up in and refluxed with methanol (5 ml); the methanolic solutions were evaporated to dryness and the residues were taken up in CH_2Cl_2 and water; the CH_2Cl_2 solutions were worked up as described above (Method E). [Method E was applied in those cases where considerable amounts of the starting bromide (**1a**) remained unchanged, in order to convert the latter into its methanolysis product (**1d**)]. If the hydroxymethyl derivative (**1g**) was present among the products, the dry residue of the CH_2Cl_2 solution (obtained according to Method D) was worked up by column chromatography (Kieselgel 60, 0.063—0.200 mm; benzene–acetone, 100:1) (Method F).

All products [(**1c**),[2,3,14] (**1d**),[2,3] (**1e**),[15] (**1g**),[4] (**2a**),[2,3] (**2b**),† and (**2c**)†] were known compounds and were identified by comparison (R_F, i.r.) with authentic samples.

Thermolysis of the Phenylazo Derivative (**1f**) *in the Presence of Lithium Bromide.*—A mixture of compound (**1f**) (0.50 g, 1.46 mmol), LiBr (127 mg, 1.46 mmol), and acetone-free DMP (5 ml) was refluxed for 4 h and worked up according to Method F (see above) to obtain, among other products (which were not studied further), compound (**1c**) (72 mg, 21%) and compound (**1g**) (71 mg, 18%), identified by comparison with authentic samples.

Reaction of 2-*Bromo*-NN-*dimethyl*-2,2-*diphenylacetamide* (**1a**) *with Sodium Methoxide in Acetone-free DMP in the Presence of* N-(2,2-*Diphenylacetyl*)*pyrrolidine* (**12**).—(*a*) Compounds (**1a**) (250 mg, 0.79 mmol) and (**12**) (210 mg, 0.79 mmol) were refluxed with a suspension of sodium methoxide (0.34 g, 6.3 mmol) in acetone-free DMP (5 ml) for 5 h with continuous stirring. The mixture was evaporated to dryness and worked up according to Method C to obtain a mixture (154 mg) of the reduction product (**1c**) and compound (**12**) which was not studied further, a mixture (69 mg) of dimers and a mixture (36 mg) of trimers (not studied further).

The ^1H n.m.r. and mass spectra of the dimeric fraction proved to be the weighted sum of the spectra of the pure dimers (**2a**) and (**13**)—(**15**) described in ref. 3.

(*b*) Compounds (**1a**) (1.0 g, 3.14 mmol) and (**12**) (0.83 g, 3.14 mmol) were stirred with a suspension of sodium methoxide (0.68 g, 12.6 mmol) in a mixture of acetone-free DMP (20 ml) and acetone (0.70 ml, 9.5 mmol) for 2 h at room temperature. Work-up as described in (*a*) furnished a dimeric fraction (0.20 g, 26%) which proved to be pure dimer (**2a**).

Reaction of 2-*Bromo*- (**1a**) *and* 2-*Chloro*-NN-*dimethyl*-2,2-*diphenylacetamide* (**1b**) *with Sodium Methoxide in Refluxing DMP.*—Compounds (**1a** or **b**) were refluxed with the suspension of sodium methoxide in acetone-free DMP or in mixtures of acetone-free DMP and acetone with continuous stirring; for details, see Table 3. Except in run 3, the resulting mixtures were worked up according to Methods A or C by t.l.c. In experiment 3 t.l.c. proved unnecessary: the dry residue of the reaction mixture turned crystalline when triturated with water. All products were known compounds and were identified by comparison of their R_F values, i.r. spectra, and (in experiment 3) their m.p.s with authentic samples.

* The symbols d and s refer to the off-resonance spectra.

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